Environment Canada
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ENVIRO

Technical

Information for

Problem

Spills

NITRIC ACID

April 1985

Canada

86-05880/

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

EnviroTIPS manuals are available from:

Publications Section
Environmental Protection Service
Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

NITRIC ACID

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

April 1985

© Minister of Supply and Services Canada 1985
Cat. No. En 48-10/50-1985E
ISBN 0-662-14226-8
BEAUREGARD PRESS LIMITED

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

NITRIC ACID (HNO_3)

Colourless to light yellow or brown, watery liquid with a choking odour.

SYNONYMS

White Fuming Nitric Acid (WFNA), Red Fuming Nitric Acid (RFNA), Nitrous Fumes, Azotic Acid, Hydrogen Nitrate, Aqua Fortis, Acide Nitrique (Fr.)

IDENTIFICATION NUMBERS

UN. No. 1760 (<40 percent acid), 2031 (>40 percent acid), 2032 (red fuming); CAS No. 7697-37-02; OHM-TADS No. 7216816; STCC No. 4918528 (>40 percent acid), 4918529 (fuming), 4930242 (<40 percent acid)

GRADES & PURITIES

40°Be, 61.4 percent HNO_3,
42°Be, 67.2 percent HNO_3,
Red and white fuming nitric acid

IMMEDIATE CONCERNS

Fire: Not combustible, but may cause ignition of combustible materials on contact.

Human Health: Highly toxic by ingestion, inhalation and skin contact. Corrosive to tissues.

Environment: Harmful to aquatic life and to land and air species.

PHYSICAL PROPERTY DATA

	100 percent	40°Be	42°Be	WFNA	RFNA
State (15°C, 1 atm):	Liquid	Liquid	Liquid	Liquid	Liquid
Boiling Point:	82.6°C	120.0°C	117.8°C	84°C	64.2°C
Melting Point:	-41.6°C	≈-24.5°C	≈-32.0°C	-41.6°C	-52°C
Flammability:	not combustible	not combustible	not combustible	not combustible	not combustible
Vapour Pressure:	6.0 kPa (20°C)	0.4 kPa (24°C)	0.91 kPa (20°C)	8.3 kPa (20°C)	18.6 kPa (25°C)
Density (g/mL):	1.50 (25°C)	1.38 (16°C)	1.41 (15°C)	1.50 (25°C)	1.55 (25°C)
Solubility (in water):	miscible	miscible	miscible	-	-
Behaviour (in water):	sinks and mixes, producing heat and toxic and corrosive fumes				
Behaviour (in air):	vapours are heavier than air				

ENVIRONMENTAL CONCERNS

Nitric acid is toxic to aquatic life due to acidity (pH effects). The nitrate ion is toxic to land and air species.

HUMAN HEALTH

TLV•: 2 ppm (5 mg/m^3) (inhalation)
IDLH: 100 ppm

Exposure Effects

Inhalation: Inhalation will cause irritation of mucous membranes and respiratory tract. In extreme cases, inhalation of nitric acid may cause pulmonary edema and death.

Contact: Contact with the skin will cause irritation, discoloration, burns, and possible ulcers and necrosis. Contact with eyes will cause irritation, conjunctivitis, burns, corneal opacity and possible blindness.

Ingestion: Ingestion of small amounts of concentrated nitric acid may cause death.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE, OXIDIZER, POISON". Call fire department and notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and inhalation of vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible. Use water spray to cool containers involved in a fire to prevent rupture and to absorb liberated nitrogen oxides.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Neutralize contaminated soil with lime, sodium bicarbonate or soda ash.

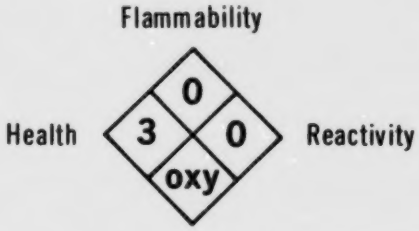
Water: Contain by damming, sand bag barriers or natural barriers. If possible, neutralize with lime, sodium bicarbonate or soda ash.

Air: Use water spray to knock down vapours. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

Category	Rating
Fire	0
Health	
Vapour Irritant	3
Liquid or Solid Irritant	4
Poison	3
Water Pollution	
Human Toxicity	3
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	4
Water	0
Self-reaction	0

NFPA
HAZARD
CLASSIFICATION



2 PHYSICAL AND CHEMICAL DATA

		Aqueous		Fuming	
	Pure 100 percent	61.38 percent (40°Be)	67.18 percent (42°Be)	WFNA	RFNA
Physical State Properties					
Appearance	Colourless (Kirk-Othmer 1981)	Transparent, colourless or pale yellow to light brown liquid (Kirk-Othmer 1981)		Colourless (CPIA 1970)	Reddish-brown (CPIA 1970)
Usual shipping state	Not commercially available (Kirk-Othmer 1981)	Liquid	Liquid	Liquid (CPIA 1970)	Liquid (CPIA 1970)
Physical state at 15°C, 101 kPa	Liquid	Liquid		Liquid (CPIA 1970)	Liquid (CPIA 1970)
Melting point	-41.6°C (Kirk-Othmer 1981)	See HNO_3•H_2O Phase Diagram		-41.6°C (CPIA 1970)	-52°C (CPIA 1970)
Freezing point	-37.62°C (HNO_3•H_2O) -18.47°C (HNO_3•$3H_2O$) (Kirk-Othmer 1981)	-24°C (Ashland 1980)	-32°C (Ashland 1980)		
Boiling point (at 101 kPa)	82.6°C (Bailar 1973) 86.0°C (Kirk-Othmer 1981)	120°C (Du Pont MSDS 1980)	117.8°C (Ashland MSDS 1977)	84°C (CPIA 1970)	64.19°C (calc.) (AFRPL 1977)
	Azeotrope: 120.5°C (68 percent by wt. HNO_3) (CRC 1982)				
Vapour pressure (kPa)	6.0 (20°C)	0.4 (24°C) (Du Pont MSDS 1980)	0.907 (20°C) (Ashland MSDS 1977)	8.34 (25°C) (CPIA 1970)	18.6 (25°C) (CPIA 1970)

		Aqueous		Fuming	
	Pure 100 percent	61.38 percent (40°Be)	67.18 percent (42°Be)	WFNA	RFNA
Decomposition temperature	>-41.6°C (Kirk-Othmer 1981)	-	-	-	-
Densities					
Density (kg/m^3)	Liq.: 1512.9 (20°C) (Kirk-Othmer 1981)	-	-	1503 (25°C) (CPIA 1970)	1550 (25°C) (CPIA 1970)
	Sol.: 1895 (-41.6°C) (Bailar 1973)	-	-	-	-
Specific gravity, liquid	1.5027 (25°C) (CRC 1982)	1.3810 (15.5°C) (Ashland 1977)	1.4078 (15.5°C) (Ashland 1977)	-	-
Specific gravity, vapour relative to air	-	-	-	3 (CPIA 1970)	-
Specific gravity, azeotrope		1.41 (20°C) (CRC 1982)			
Fire Properties					
Flammability	Non-combustible	Noncombustible		Noncombustible	
Decomposition temperature	See Physical State Properties	-	-	-	
Decomposition products	Nitrogen oxides - primarily NO_2				
Behaviour in a fire	Decomposition products support combustion; increases the flammability of combustible, organic or other readily oxidizable materials; can cause ignition of some materials (NFPA 1978; CPIA 1970)				

		Aqueous		Fuming	
	Pure 100 percent	61.38 percent (40°Be)	67.18 percent (42°Be)	WFNA	RFNA
Other Properties					
Molecular weight of pure substance	63.01 (CRC 1980)	-	-	-	57.2 (AFRPL 1977) (nominal molecular weight of mixture)
Chemical formula	HNO_3	-	-	-	$H_{0.8894}$ $N_{0.9365}$ $O_{2.6989}$
Constituent components of typical commercial grade	Not available	61.4 to 62.4 percent	67.2 to 68.2 percent	97.5 percent HNO_3, 0.5 percent NO_2 max., 2.0 percent H_2O max.	82.4 to 85.4 percent HNO_3, 14± 1.0 percent NO_2, 1.5 to 2.5 percent H_2O
Refractive index	1.397 (16.4°C) (CRC 1980) 1.4030 (5°C) (Bailar 1973)	-	-	-	-
Viscosity, liquid	0.9 mPa·s (20°C) (Kirk-Othmer 1981)	2.0 mPa·s (60 percent) (20°C) (Kirk-Othmer 1981)	2.0 mPa·s (70 percent) (20°C) (Kirk-Othmer 1981)	0.733 mPa·s (25°C) (CPIA 1970)	1.231 mPa·s (25°C) (calc.) (AFRPL 1977)
Liquid surface tension	41.5 mN/m (20°C) (Bailar 1973) 42.7 mN/m (98.5 percent) (11.6°C) (CRC 1980)	-	-	-	40.13 mN/m (25°C) (calc.) (AFRPL 1977)

	Pure 100 percent	Aqueous 61.38 percent (40°Be)	Aqueous 67.18 percent (42°Be)	Fuming WFNA	Fuming RFNA
Hygroscopicity	Hygroscopic (MCA 1961)				
Latent heat of fusion	166.3 kJ/kg, 216.3 kJ/kg ($HNO_3 \cdot H_2O$), 248.9 kJ/kg ($HNO_3 \cdot 3H_2O$) (Kirk-Othmer 1981)	-	-	-	183.2 kJ/kg (-41.6°C) (AFRPL 1977)
Latent heat of vaporization	626.6 kJ/kg (20°C) (Kirk-Othmer 1981)	-	-	-	587.8 kJ/kg (64.19°C) (calc.) (AFRPL 1977)
Heat of formation, gas	-1989 kJ/kg (0°C), -2145 kJ/kg (25°C) (Bailar 1973)	-	-	-	-
Heat of formation, liquid	-2751.1 kJ/kg (25°C) (Kirk-Othmer 1981)	-	-	-	-2759 kJ/kg (25°C) (calc.) (AFRPL 1977)
Heat of formation, $HNO_3 \cdot H_2O$	-7492 kJ/kg (25°C) (Kirk-Othmer 1981)	-	-	-	-
Heat of formation, $HNO_3 \cdot 3H_2O$	-14 100 kJ/kg (25°C) (Kirk-Othmer 1981)	-	-	-	-
Ionization potential	11.03 eV (Rosenstock 1977)	-	-	-	-

		Aqueous			
	Pure 100 percent	61.38 percent (40°Be)	67.18 percent (42°Be)	Fuming WFNA	Fuming RFNA
Heat of solution, liquid	-528.5 kJ/kg (25°C) (CRC 1982) -476.4 kJ/kg (10°C) (CRC 1957)				
Heat of dilution (to infinite dilution)					
$HNO_3 \cdot H_2O$:	-244.56 kJ/kg (Bailar 1973)				
$HNO_3 \cdot 3H_2O$:	-75.96 kJ/kg (Bailar 1973)				
Heat capacity constant pressure (C_p), gas	0.847 kJ/(kg·K) (25°C) (Bailar 1973)	-	-	-	-
constant pressure (C_p), liquid	1.76 kJ/(kg·K) (20°C) (Kirk-Othmer 1981) 1.74 kJ/(kg·K) (25°C) (Bailar 1973)	-	-	-	1.758 kJ/(kg·K) (25°C) (AFRPL 1977)
constant pressure (C_p), $HNO_3 \cdot H_2O$	2.25 kJ/(kg·K) (25°C) (Bailar 1973)	-	-	-	
constant pressure (C_p), $HNO_3 \cdot 3H_2O$	2.78 kJ/(kg·K) (25°C) (Bailar 1973)	-	-	-	

		Aqueous		Fuming	
	Pure 100 percent	61.38 percent (40°Be)	67.18 percent (42°Be)	WFNA	RFNA
Thermal conductivity	0.28 W/(m·K) (20°C) (Kirk-Othmer 1981)	0.40 W/(m·K) (20°C) (60 percent) (Kirk-Othmer 1981)	0.36 W/(m·K) (20°C) (70 percent) (Kirk-Othmer 1981)	-	0.2915 W/(m·K) (25°C) (AFRPL 1977)
Saturation concentration	165 g/m^3) (20°C) (Calculated)				
Diffusivity	2.98 x 10^{-5} cm^2/s (in water, 25°C) (Perry 1973) 2.39 x 10^{-5} cm^2/s (CRC 1957) (aqueous solution into pure H_2O) 0.1 g molecule/L (at 19.5°C)	-	-	-	-
pH of aqueous solution	4.9 (0.0032 M) (Jones 1969) 1.0 (0.1 M, calculation based on ~93 percent ionized (Cotton 1972) 1.0 (0.1 M, based on acidity function values, H_o (25°C) (Paul 1957; Bell 1959) 0.6 (0.25 M, based on acidity function values, H_o (25°C) (Paul 1957; Bell 1959) 0.2 (0.5 M, based on acidity function values, H_o (25°C) (Paul 1957; Bell 1959)				
Eutectic compositions (aqueous)		32.7 percent, f.p. -43°C (Lange's Handbook 1979)			

	Pure 100 percent	Aqueous 61.38 percent (40°Be)	Aqueous 67.18 percent (42°Be)	Fuming WFNA	Fuming RFNA
Eutectic compositions (aqueous) (Cont'd)		~71 percent, f.p. ~-41°C (Kirk-Othmer 1981) ~91 percent, f.p. ~-60°C (Kirk-Othmer 1981)			
Critical pressure	-	-	-	-	8.34 mPa (calc.) (AFRPL 1977)
Critical temperature	-	-	-	-	273.33°C (calc.) (AFRPL 1977)
Coefficient of cubical expansion	0.00124 (20°C) (Raznjevic 1976)	-	-	-	-
Trouton's constant	88.76 kJ/kg (Bailar 1973)	-	-	-	-
Dielectric constant	50 ± 10 (Bailar 1973)	-	-	-	-
Specific conductance	3.72 x 10^{-2} ohm^{-1} cm^{-1} (Bailar 1973)	-	-	-	-
Solubility					
Water	Miscible in all proportions (Kirk-Othmer 1981)				

	Pure 100 percent	Aqueous 61.38 percent (40°Be)	Aqueous 67.18 percent (42°Be)	Fuming WFNA	Fuming RFNA
Other Materials	Reacts violently in ethanol, soluble in diethylether (CRC 1980)				
Vapour Weight-to-Volume Conversion Factor	1 ppm = 2.619 mg/m^3 (20°C) (Verschueren 1984)				

The Chemistry of Nitric Acid

Pure nitric acid is a colourless liquid or a white crystalline solid. The former has a freezing point of -41.59°C, but decomposes above this temperature according to the equation:

$$2HNO_3 \rightarrow 2NO_2 + H_2O + 1/2\ O_2$$

Gas phase decomposition also occurs according to the above equation. It has long been known that the decomposition of compounds containing nitrogen and oxygen may be further complicated by the setting up of other equilibria. One such mechanism is based on the dehydration of the acid:

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

followed by the normal first order decomposition of dinitrogen pentoxide:

$$N_2O_5 \rightarrow NO_2 + NO_3$$
$$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$$
$$NO + N_2O_5 \rightarrow 3NO_2 \text{ or } NO + NO_3 \rightarrow 2NO_2$$

An alternate mechanism involves OH radicals:

$$HNO_3 \rightarrow NO_2 + OH$$
$$OH + HNO_3 \rightarrow NO_3 + H_2O$$

$$NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO$$
$$NO + NO_3 \rightarrow 2NO_2$$

The solid is quite stable, but the liquid degenerates to a limited extent at any temperature above its melting point and turns yellow within an hour at room temperature. Even the normal concentrated aqueous acid, approximately 70 percent by weight nitric acid, is colourless initially but often becomes yellow to brown as a result of photochemical decomposition which produces nitrogen dioxide according to the above equation. The pure material has the highest self-ionization of the pure liquid acids:

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

which is followed by rapid loss of water:

$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$

Therefore, the overall self-dissociation is represented by the equation:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

(Cotton 1972; Bailar 1973; Jolly 1964; Kirk-Othmer 1981). Other authors indicate that self-ionization proceeds through the equations:

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5 \rightleftharpoons H_2O + NO_2^+ + NO_3^-$$

followed by further ionization (Bailar 1973):

$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$

The acid is completely miscible with water and is most commonly known and used as the aqueous solution, sometimes with the addition of dissolved nitrogen dioxide. In dilute aqueous solutions, nitric acid is a completely strong acid, i.e., completely ionized (Vanderwerf 1961; Jolly 1964). Another reference states the acid is approximately 93 percent dissociated at 0.1 M and is considered a strong, monobasic acid (Cotton 1972). Raman spectra of nitric acid solutions indicate ionization is incomplete at concentrations as low as 3 M and that a large fraction of the acid is in the form of HNO_3 molecules at higher concentrations. Actual measurements show the degree of ionization to be about 100 percent at 1 molal, 98 percent at 2 molal, 90 percent at 4 molal, 50 percent at 15 molal and about 30 percent at 23 molal, indicating clearly that nitric acid behaves as a completely strong acid at low concentrations, but as a partially ionized acid at higher concentrations (McKay 1956). It has been demonstrated to be a much weaker acid than

the other strong acids like sulphuric (H_2SO_4), hydrochloric (HCl), hydrobromic (HBr) and perchloric ($HClO_4$) acids in nonaqueous solvents of low dielectric constant such as acetic acid (CH_3COOH) (Jolly 1964). Acidity function (H_o) plots of nitric acid at various molarities up to 7, when compared to those of the strong acids mentioned above, show acidities considerably less than the others which are grouped closely together. At molarities less than about 0.9, the curves merge, indicating the acid does indeed behave as a strong acid in dilute solutions. The acidity function equation for nitric acid is:

$$-H_o = \log \alpha m - 4 \log (1 - 0.072\, \alpha m) + 3 \log (1 + 0.032\, m)$$

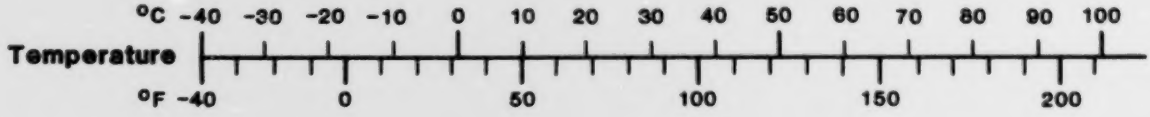
where α is the degree of dissociation and m is the concentration, in molality (Bell 1959).

Two hydrates, monohydrate ($HNO_3 \cdot H_2O$) and trihydrate ($HNO_3 \cdot 3H_2O$), may be crystallized from aqueous solution. The former has a melting point of -37.62°C and corresponds to 77.77 percent by weight acid; the latter melts at -18.47°C and corresponds to 53.83 percent by weight acid. Raman spectra of the former show that it exists as hydronium nitrate ($H_3O^+NO_3^-$). The existence of a dimer hydrate ($2HNO_3 \cdot 3H_2O$) has also been confirmed (Cotton 1972; Bailar 1973; Jolly 1964; Kirk-Othmer 1981).

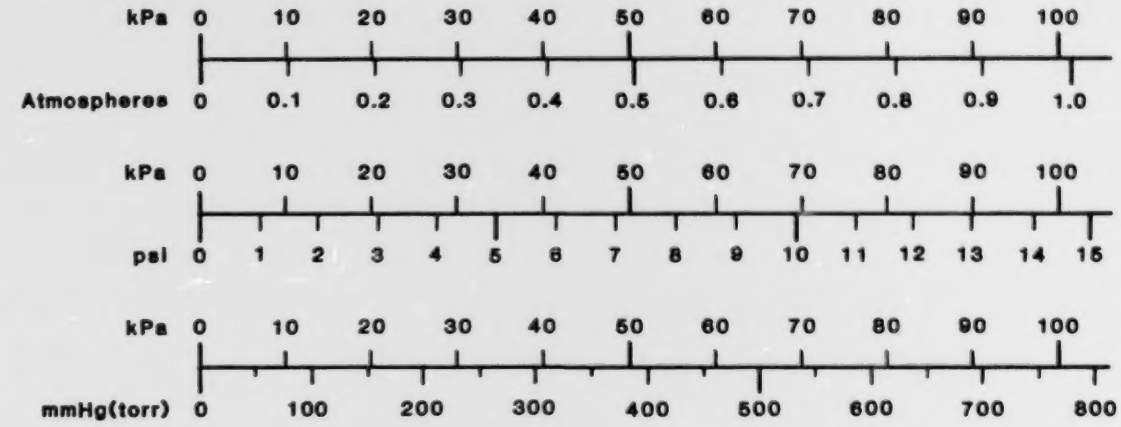
Nitric acid is a strong oxidizing agent, but both the rate of its reactions and its reduction products are strongly influenced by concentration. Its activity as an oxidizing agent is also apparently dependent upon the presence of free nitrogen oxides. For example, concentrations below 2 M have little oxidizing power, while the concentrated acid is a powerful oxidizing agent with only the metals gold, platinum, rhodium and iridium not being attacked, and aluminum, iron and copper being rendered passive. Only magnesium liberates hydrogen and then only initially from dilute acid. In solutions that are less than 1 M in concentration, iodine is formed only very slowly from iodide solution, while at concentrations greater than 2 M, iodine, bromine and chlorine are rapidly liberated from halide salts. Pure nitric acid does not attack copper; however, when oxides of nitrogen are introduced, the reaction at first is slow and then proceeds rapidly and violently. The reduction products of nitric acid, as mentioned above, vary with the concentration of the acid and the strength of the reducing agent with which it reacts. Dilute nitric acid tends to give a predominance of nitric oxide (NO); concentrated acid produces a mixture that is richer in nitrogen dioxide (NO_2), but a mixture is generally produced. Very dilute nitric acid, when reacted with a strong reducing agent such as metallic zinc, produces a mixture of ammonia (NH_3) and hydroxylamine (NH_2OH). The acid also reacts with organic compounds where it serves neither as an oxidizing agent nor as a source of hydrogen ions (Jolly 1964; Kirk-Othmer 1981; Cotton 1972).

Fuming nitric acid is concentrated nitric acid that contains dissolved nitrogen dioxide (NO_2). The so-called red fuming nitric acid contains an amount in excess of that which can be hydrated to nitric acid (HNO_3) and nitric oxide (NO). The vapour pressure and density of such solutions increase with the percentage of nitrogen dioxide present. For example, an acid containing about 45 percent by weight nitrogen dioxide and 55 percent by weight nitric acid has a vapour pressure of 101 kPa (760 mm of mercury) at 25°C and a density of 1640 kg/m^3. Samples containing NO_2/HNO_3 percentage ratios of 14 ± 1.0/82.4 to 85.4 and 0.5/97.5 (the remainder essentially water) have vapour pressures of 18.6 and 8.34 kPa, respectively and densities of 1550 and 1503 kg/m^3, respectively. The fuming acids are colourless to yellow or reddish-brown. They are generally clear, strongly fuming (RFNA), corrosive liquids which evolve nitric acid vapour and the vapours of nitrogen oxides. They are strong oxidizing agents, will vigorously attack most metals, and react with many organic materials, spontaneously causing fire. The materials are hygroscopic and will react with seawater, releasing large quantities of nitrogen oxides. The fuming acids are soluble in water in all proportions, with accompanying evolution of heat and oxides of nitrogen (Cotton 1972; Kirk-Othmer 1981; CPIA 1970).

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

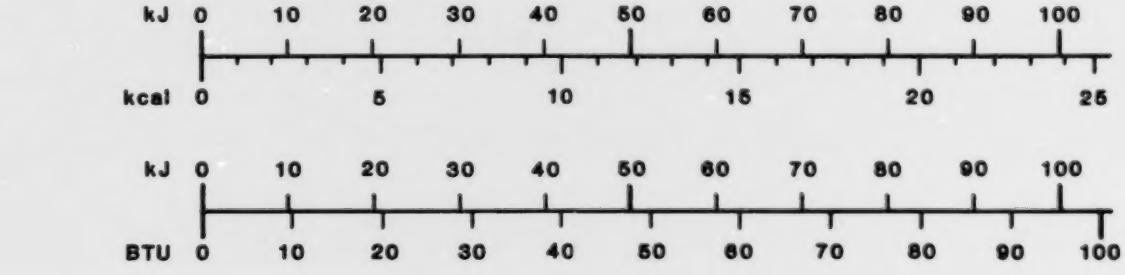
Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J



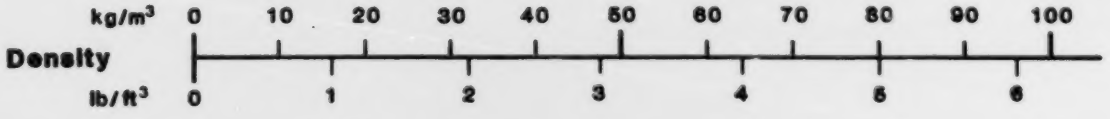


FIGURE 1

NITRIC ACID

PHASE DIAGRAM OF THE $HNO_3 \cdot H_2O$ SYSTEM

Reference: KIRK-OTHMER 1981; LINKE 1958

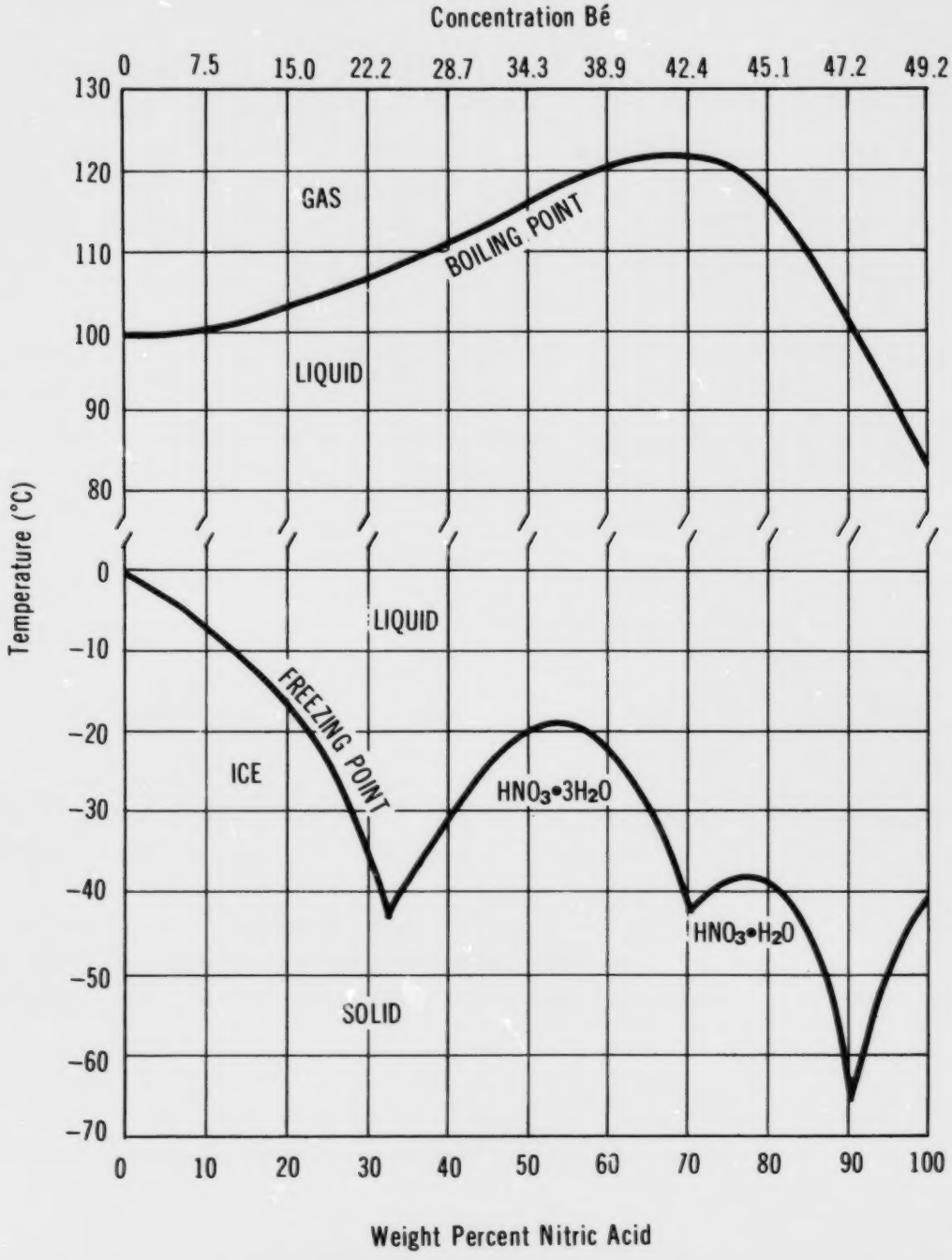


FIGURE 2

NITRIC ACID (100%)

VAPOUR PRESSURE vs TEMPERATURE

Reference: KIRK-OTHMER 1981; CRC 1982

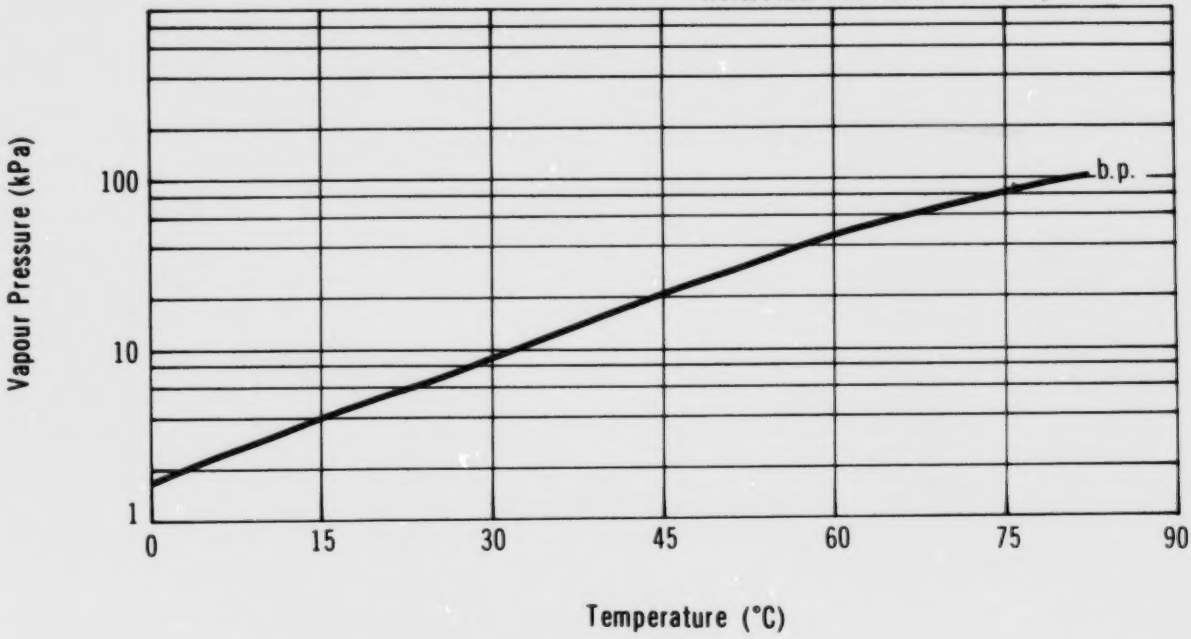


Figure 3

NITRIC ACID (100%)

LIQUID DENSITY vs TEMPERATURE

Reference: BAILAR 1973

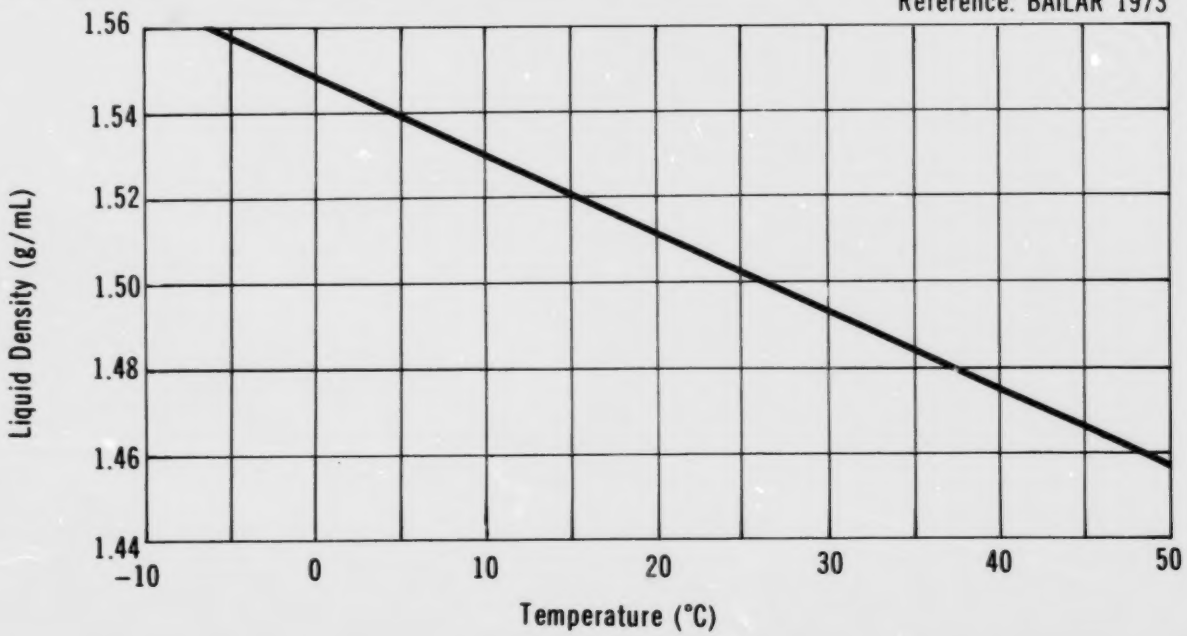


FIGURE 4

NITRIC ACID

DENSITY OF SOLUTIONS

Reference: KIRK-OTHMER 1981

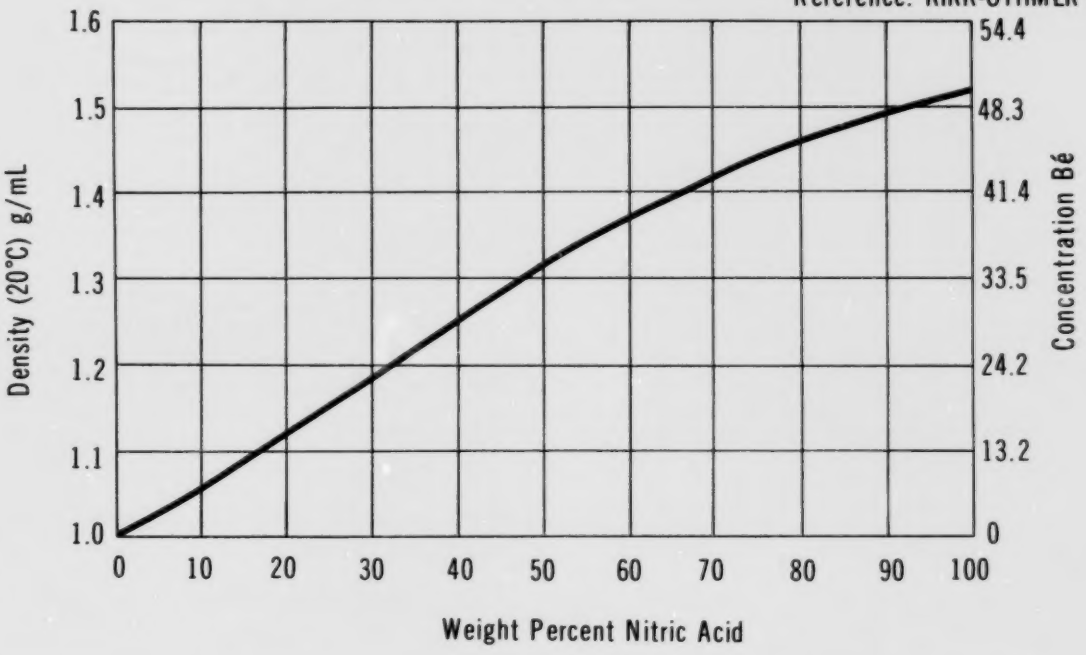


FIGURE 5

NITRIC ACID

VISCOSITY OF SOLUTIONS

Reference: KIRK-OTHMER 1981

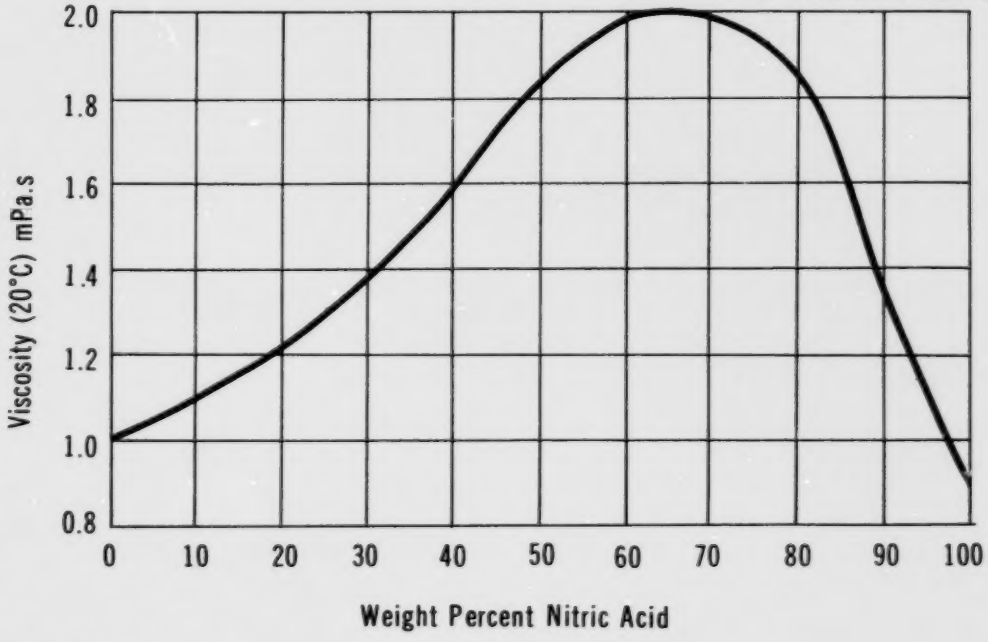
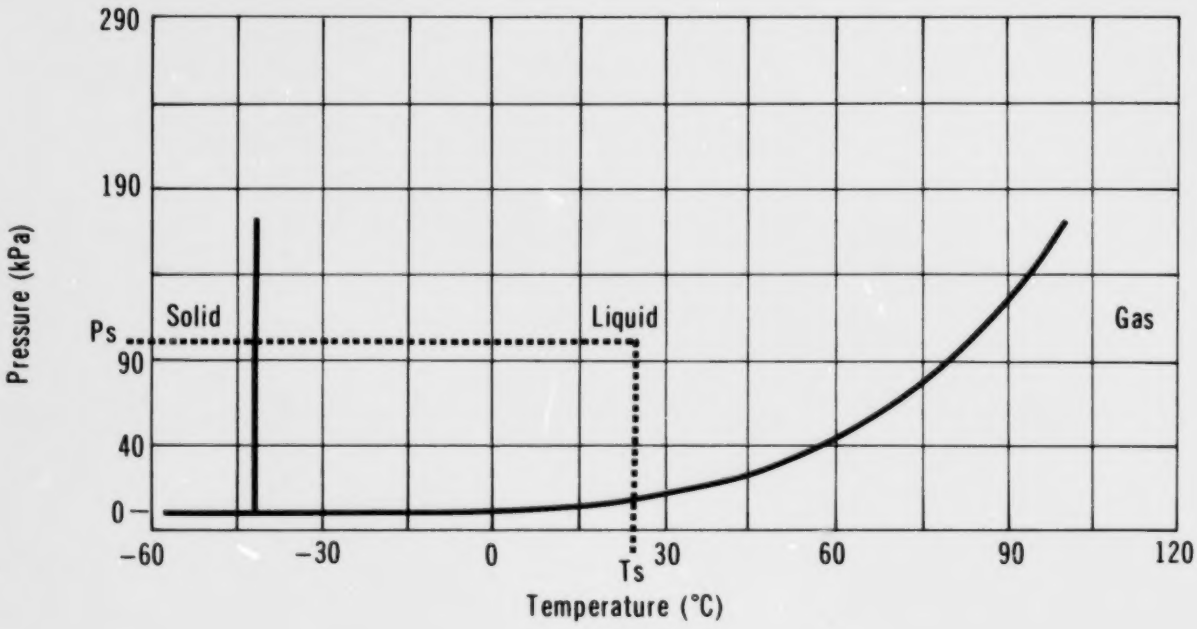


FIGURE 6

NITRIC ACID (100%)

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Corpus 1984; Ashland TD 1980)

Nitric acid is sold in 40°Be and 42°Be grades (61.38 and 67.18 percent), as well as occasionally in red and white fuming grades.

3.2 Domestic Manufacturers (Corpus 1984; CBG 1980)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Canadian Industries Ltd.
90 Sheppard Avenue East
North York, Ontario
M2N 6H2
(416) 226-6110

Cominco
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

Cyanamid Canada
2255 Sheppard Avenue East
Willowdale, Ontario
M2J 4Y5
(416) 498-9405

Du Pont Canada
Box 2200, Streetsville
Mississauga, Ontario
L5M 2H3

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Genstar Chemical Limited
1255 rue Université, suite 1420
Montréal, Quebec
H3B 3X1

Nitrochem Inc.
Suite 800, 2055 Peel Street
Montreal, Quebec
H3A 1V4
(514) 849-9222

Simplot Chemical
P.O. Box 940
Brandon, Manitoba
R7A 6A1
(204) 728-5701

Valleyfield Chemical Products
P.O. Box 5520
Valleyfield, Quebec
J6S 4V9
(514) 371-5520

Western Co-operative Fertilizers
11111 Barlow Street S.E.,
P.O. Box 2500
Calgary, Alberta
T2P 2N1
(403) 279-4421

3.3 Other Supplier (CBG 1980; Scott 1979)

Monsanto Canada Inc.,
2000 Argentia Road, Plaza 2
3rd Floor
Mississauga, Ontario
L5M 2G4
(416) 826-9222

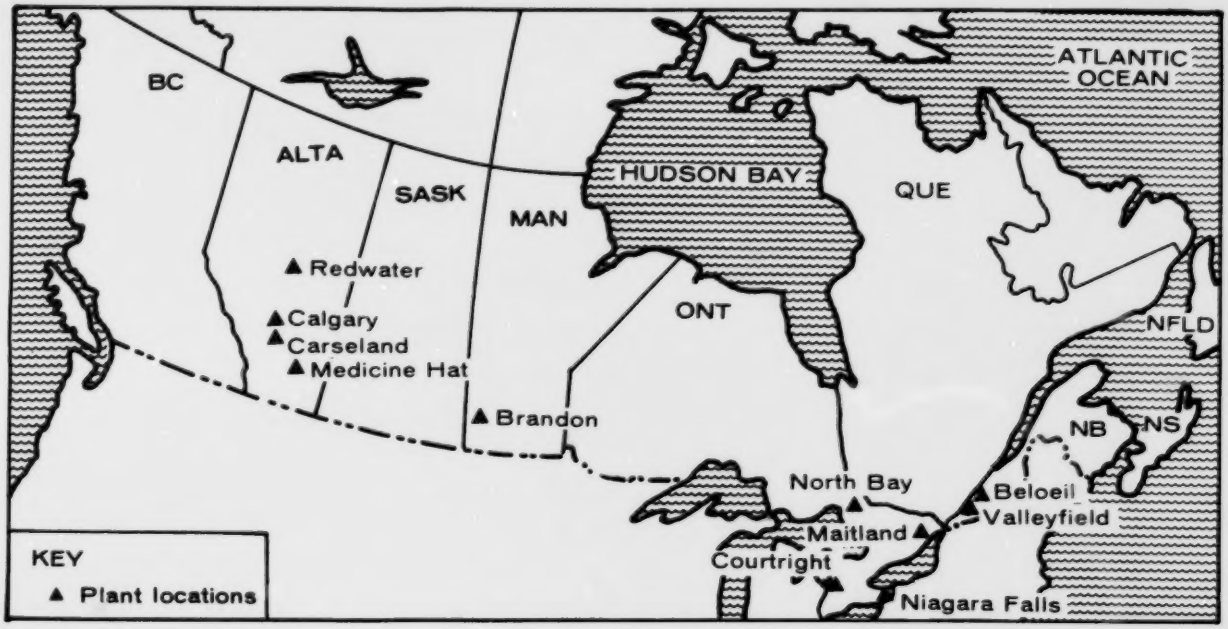
3.4 Major Transportation Routes

Current Canadian production of nitric acid is located primarily in Ontario, at Maitland, Niagara Falls and Courtright (40 percent of capacity) and in Alberta, at Carseland, Redwater, Calgary and Medicine Hat (60 percent of capacity). Other production facilities are in Quebec and Manitoba. Transportation is fairly widespread across Canada, although most of the product is used in or near the plant for ammonium nitrate production. Figure 7 shows production sites in Canada.

FIGURE 7

NITRIC ACID

CANADIAN PRODUCERS



3.5 Production Levels (Corpus 1984)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
C-I-L, Beloeil, Que.	60
C-I-L, Nobel, Ont.*	16.5
C-I-L, Courtright, Ont.	90
C-I-L, Carseland, Alta.	180

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Cominco, Calgary, Alta.	51
Cyanamid Canada, Niagara Falls, Ont.	160
Du Pont Canada, North Bay, Ont.	18
Esso Chemical Canada, Redwater, Alta.	150
Nitrochem, Maitland, Ont.	227
Simplot Chemical, Brandon, Man.	110
Valleyfield Chemical Products, Valleyfield, Que.	40
Western Cooperative Fertilizers, Medicine Hat, Alta.	85
Western Cooperative Fertilizers, Calgary, Alta.	65
TOTAL	1252.5
Domestic Production (1982)	1020
Imports (1982)	0.5
TOTAL SUPPLY	1020.5

* Plant closed in 1983.

3.6 Manufacture of Nitric Acid (FKC 1975; Kirk-Othmer 1981; Bailar 1973)

3.6.1 General. Almost all of the nitric acid produced commercially is obtained by the oxidation of ammonia. The method, despite operational variations, consists of three basic steps: oxidation of ammonia to nitric oxide (NO), oxidation of nitric oxide to nitrogen dioxide (NO_2), and absorption of nitrogen oxides in water to produce nitric acid and additional nitric oxide.

3.6.2 Raw Materials. Anhydrous ammonia and air or pure oxygen are the raw materials used in the manufacture of nitric acid.

3.6.3 Manufacturing Process. In the initial reaction, ammonia is oxidized with excess oxygen over a platinum-rhodium catalyst, which has a high specificity in promoting the oxidation to nitric oxide (equation 1) rather than the thermodynamically more favourable reaction to nitrogen. The competing equations are as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \Delta H_{298} = -226 \text{ kJ/mole} \qquad (1)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H_{298} = -317 \text{ kJ/mole} \qquad (2)$$

The catalyst normally preferred is composed of platinum with 5 to 10 percent by weight rhodium added and sometimes 5 percent by weight palladium. The catalyst is woven into a fine mesh gauze. Under normal operating conditions, 95 to 98 percent of the ammonia feed is converted to nitric oxide according to equation 1. The reaction efficiency is measured as the percent of the ammonia feed which produces nitric acid.

Efficiency increases with the temperature of the gauze and is generally quoted as ≈97 percent at 850°C and 101 kPa, and ≈93 percent at 900°C and 0.4 MPa, with industrial experience generally showing little dependence on pressure. Usual acceptable industrial efficiency values are 98 percent at 850°C and 101 kPa, and 96 percent at 900°C and 0.8 MPa. Contact time of ammonia and catalyst is usually about 10^{-3} s.

In the second step, nitric oxide is converted to nitrogen dioxide by reacting the gas with oxygen according to the equation:

$$2NO + O_2 \rightleftharpoons 2NO_2 \qquad (3)$$

The equilibrium constant for the reaction favours the production of nitrogen dioxide at lower temperatures. Below 150°C, almost all nitric oxide combines with any oxygen that is present if sufficient reaction time is allowed. The rate of reaction is slow and decreases with increasing temperature; therefore, there is a major advantage in using lower temperatures to speed the reaction. Pressure also has a dramatic effect on the oxidation process; the volume required to effect the oxidation of a given percentage of nitric oxide in a gas mixture is inversely proportional to the cube of the pressure.

The absorption of nitrogen oxides in water is a complex reaction, with many uncertainties; however, the overall reaction is usually shown such that only the nitrogen dioxide present in the gas reacts with liquid water:

$$3NO_{2(g)} + H_2O_{(l)} \rightleftharpoons 2HNO_{3(aq)} + NO_{(g)} \qquad (4)$$

It is pointed out, however, that nitrogen dioxide dimerizes immediately to an equilibrium mixture with dinitrogen tetroxide:

$$2NO_2 \rightleftharpoons N_2O_4 \qquad (5)$$

Lower temperatures and increasing pressures favour a shift to the right in equation 5. By equation 4 one can easily see the oversimplification of the absorption process. Some studies assume the major reaction species is dinitrogen tetroxide, since the reported equilibrium data can be fairly well correlated by $P_{NO}/(P_{N_2O_4})^{1.5}$ as a function of acid concentration independent of temperature. In the end, though, principles of equipment design can be deduced from equation 4 and the available equilibrium data. Generally, equipment sizes can be decreased to produce a given amount and concentration of acid; more of a higher concentration of acid can be produced by reducing operating temperatures, increasing operating pressures, increasing the proportion of NO_2/NO in the

feed gas, and increasing the reaction volume after vapour-liquid contact to permit reoxidation of nitric oxide (equation 4).

Many variations in plants exist. In a typical plant, air is compressed to about 0.86 MPa (110 psig), preheated to about 250°C, and mixed with ammonia vapour. The mixture, containing about 10 percent ammonia, by volume flows down through a pack of flat catalyst gauzes, producing nitric oxide at about 95 percent efficiency at about 930°C. The hot gas bearing the converter is cooled by exchange with the feed air and in a tail-gas reheater before moving to a water-cooled condenser. Any weak acid that is produced in the condenser is pumped to an intermediate tray in the absorption tower; the uncondensed process gas moves to the bottom of the tower. The absorption tower consists of a series of bubble-cap trays provided with cooling coils. As the gas flows up the tower countercurrent to the acid flow, nitrogen dioxide dissolves in the water, forming nitric acid and nitric oxide. The latter is reoxidized in the space between the trays by the excess oxygen present in the system. Steam condensate is added as the absorbent at the top of the tower. Dissolved nitrogen oxides are removed from the product acid by contact with secondary air in a bleaching tower. The tail gas leaving the absorption tower is reheated to about 250°C by exchange with the process gas and then is expanded through a gas engine which provides about 40 percent of the power required to drive the reciprocating air compressors. Fume abatement is accomplished in modern plants by absorption towers usually equipped with a refrigeration system to reduce the size of the tower.

The nitric acid produced by the standard ammonia oxidation process is in aqueous solution at a concentration of 50-70 percent by weight. The acid can be concentrated to 98-99 percent by weight by distillation from 93 percent sulphuric acid. The condensed nitric acid usually contains less than 0.1 percent by weight lower oxides. The pure acid can be obtained by treating potassium nitrate (KNO_3) with 100 percent sulphuric acid at 0°C and removing the nitric acid by vacuum distillation (Cotton 1972).

The American Chemical Society specifies the concentration of reagent-grade nitric acid to be 69.0 to 71.0 percent by weight nitric acid plus other specifications. Fuming nitric acid must contain no less than 90 percent by weight nitric acid and no more than 0.1 percent by weight dissolved oxides. The U.S. Department of Defence lists the ACS grades for both as standard as well as having a technical grade with a minimum of 61 percent by weight nitric acid plus other specifications. Other classes (5) are specified for the manufacture of explosives. Reference to fuming nitric acid, therefore, pertains to

the ACS specifications previously discussed, and reference to WFNA and RFNA pertains to the U.S. military designation.

3.7 Major Uses in Canada (Corpus 1984)

Nitric acid is used for production of ammonium nitrate, ammonium nitrate phosphate, high explosives, nylon intermediates, uranium extraction, lead pigments, and metal nitrates. In 1982, 82 percent of domestic production was used for ammonium nitrate production, 7 percent was used for nylon intermediates, and 5 percent was used for ammonium nitrate phosphate production.

3.8 Major Buyers in Canada (Corpus 1984; CBG 1980)

A & B Chemical Products, Stoufville, Ont.
Agnew Lake Mines, Agnew Lake, Ont.
Allied Chemical Canada Ltd., Corunna, Amherstburg, Ont.; Montreal, Que.
Anachemia Chemical, St. Jerome, Que.
Arliss Chemical Inc., Mississauga, Ont.; Montreal, Que.
BASF Chemical Inc., Montreal, Que.
Bayer (Canada) Ltd., Montreal, Que.
Benson Chemicals Ltd., Freelton, Ont.
Canada Colors & Chemicals, Don Mills, Ont.
Canadian Hanson, Toronto, Ont.
Denison Mines, Elliot Lake, Ont.
Eldorado Nuclear, Port Hope, Ont.
Hercules Canada, St. Jean, Que.
International Chemical Ltd., Brampton, Ont.
M & T Chemicals Ltd., Hamilton, Ont.
Mallinckrodt, Montreal, Que.
Reed, Ajax, Ont.
Rio Algom Mines, Elliot Lake, Ont.
Shefford Chemicals Ltd., Granby, Que.
Uba Chemical Industries Ltd., Mississauga, Ont.
Van Waters & Rogers, Vancouver, B.C.; Montreal, Que.
Winfield Chemical Ltd., Woodstock, N.B.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Nitric acid solutions are occasionally shipped bulk in specially designed railway tank cars and tank motor vehicles.

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of nitric acid are listed in Table 2. Figure 8 shows a 103CW railway car for nitric acid service. Table 3 indicates railway tank car details associated with this drawing. Nitric acid cars are never unloaded through bottom outlets; these are prohibited. The cars are unloaded from the top using compressed air or pump (MCA 1961). The acid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with a 51 mm (2 in.) unloading flange.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
103AALW	Aluminum fusion-welded tank with dome. Uninsulated or insulated. 1% dome. Top unloading arrangement required. Bottom outlet prohibited; bottom washout optional. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Nitric acid (80 percent or more).
103CW	Alloy (stainless) steel fusion-welded tank with dome. Insulated or uninsulated. 1% dome. Bottom outlet or washout prohibited. Top unloading arrangement required. Safety valve (242 kPa) (35 psi). Nitric acid (40 percent or more).
105A100ALW	Aluminum fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Bottom outlet or washout prohibited. Safety valve (518 kPa) (75 psi). Nitric acid (90 percent or more).

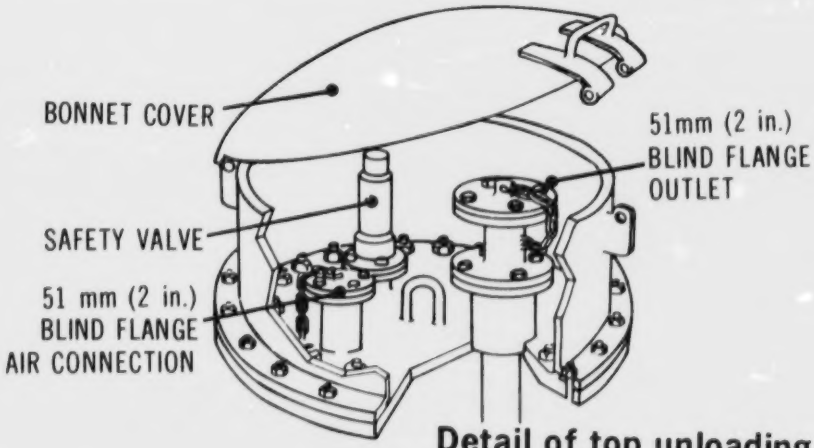
* Canadian Transport Commission and Department of Transportation (U.S.)

FIGURE 8

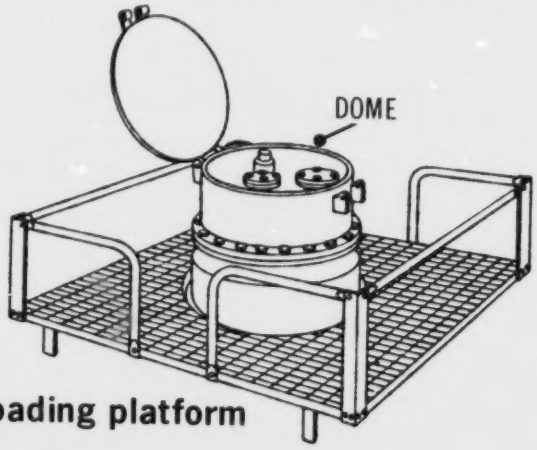
NITRIC ACID

RAILWAY TANK CAR - CLASS 103CW

Reference: TCM 1979; RTDCR 1974



Detail of top unloading arrangement



Detail of loading platform

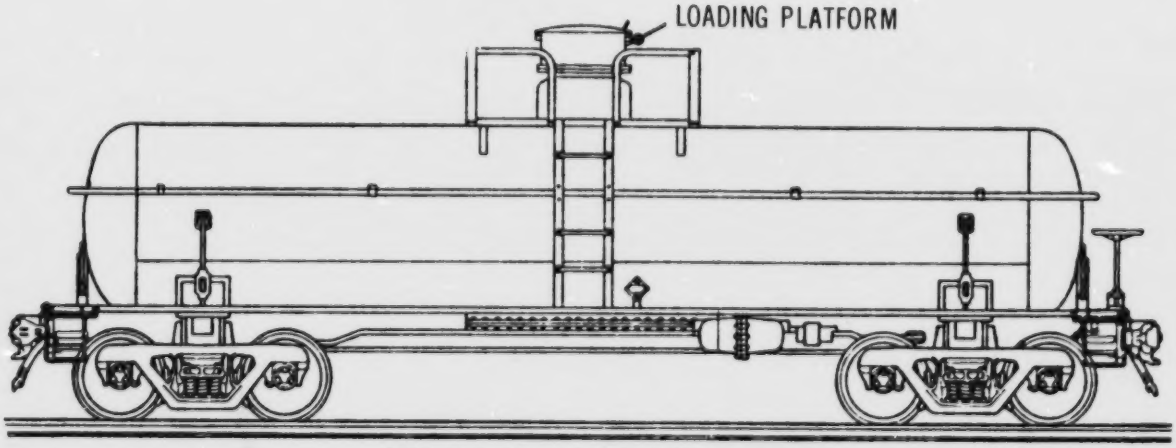


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 103CW (TCM 1979; RTDCR 1974)

Description	Dimension
Overall	
Nominal capacity	30 300 L (6700 gal.)
Car weight - empty	19 800 kg (43 700 lb.)
Car weight - max.	80 300 kg (177 000 lb.)
Tank	
Material	stainless steel
Thickness	top: 9.5 mm (3/8 in.) bottom and heads: 1.3 mm (1/2 in.)
Inside diameter	196 mm (77 in.)
Test pressure	414 kPa (60 psi)
Burst pressure	1660 kPa (240 psi)
Approximate Dimensions	
Coupled length	12.1 m (39 ft. 9-1/2 in.)
Length over strikers	11.3 m (37 ft. 2 in.)
Length of truck centres	8.0 m (26 ft. 2-1/2 in.)
Height to top of grating	3.2 m (10 ft. 7-1/2 in.)
Overall height	4.3 m (13 ft. 11-5/8 in.)
Overall width (over grabs)	3.1 m (10 ft. 2 in.)
Length of grating	2.0 m (6 ft. 8-1/2 in.)
Width of grating	1.6 m (5 ft. 2-1/8 in.)
Loading/Unloading Fixtures	
Top Unloading	
Unloading connection	blind flange, 51 mm (2 in.)
Manway/fill hole	not specifically provided
Air connection	blind flange, 51 mm (2 in.)
Bottom Unloading	
Bottom outlet	prohibited
Safety Devices	safety valve set at 241 kPa (35 psi)
Dome	required, 1 percent expansion capacity
Insulation	optional

4.1.1.2 Tank motor vehicles. The capacities of tank trucks transporting nitric acid range from 14 to 27 tonnes (PC 1982). Similar to railway tank cars, these highway tankers are unloaded from the top, usually the stand pipe being extended down over the back of the tank. Compressed air or pumping is used for unloading. The air inlet is usually a 25 mm (in.) diameter male threaded connection located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied (PC 1982).

Tank motor vehicles must conform to Transport Canada Specifications TC312, covering MC310, MC311 and MC312, as outlined in Table 4 (TDGC 1980). Nitric acid solutions are not transported under pressure. Highway tankers must be pressure tested at 311 kPa (45 psi) minimum to allow for the compressed air pressure of 207 kPa (25 psi) used during top unloading. The normal working pressure of the tanker is 242 kPa (35 psi) (PC 1982).

TABLE 4 TANK MOTOR VEHICLE SPECIFICATIONS

TC* Specification Number	Description
TC312	Stainless steel or aluminum tank. Design and construct in accordance with ASME Code when unloading by pressure in excess of 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment as required by ASME Code. One minimum 380 mm (15 in.) diameter manhole per compartment. Bottom washout optional.

* Transport Canada

4.1.2 Packaging. In addition to bulk shipments, nitric acid is also transported in drums, carboys, glass containers and portable tanks. Table 5 provides a summary of these specifications (RTDCR 1974).

TABLE 5 PACKAGING OF NITRIC ACID

Applicability to Solution Concentration	Specification Number(s)	Description
>40 percent	5C	Lined steel drum
>80 percent	42B, 5X	Aluminum drums or aluminum-lined steel drums
<72 percent	1A, 1C, 1K	Glass carboys in boxes or kegs
	1D, 1E	Glass carboys in plywood
	6o	Glass-lined portable steel tanks
	33a	Polystyrene cases with inside glass bottles not over 2.2 L (77 fl. oz.) each
	12R	Polystyrene board boxes with inside glass bottles
<90 percent	15A, 15B, 15C, 16A, 19A, 11A or 11B	Wooden boxes or barrels with inside glass containers of not more than 2.8 L (99 fl. oz.) each
>90 percent	15A, 15B, 16A, 19A, 11A	Wooden boxes or barrels with inside glass containers of not more than 2.8 L (99 fl. oz.) each

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1961):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.
- Relieve any internal pressure in the tank car through the safety valve.

Proceed with off-loading as follows (MCA 1961):

- Remove blind flange and connect the 51 mm (2 in.) unloading line to the discharge outlet at the top of the car; connect the 51 mm (2 in.) air line. Air pressure must be

reduced to 207 kPa (30 psi) for unloading. A safety relief valve must be installed in the air line to release at 242 kPa (35 psi).

- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure.
- Reverse the above procedure to close up the car.

If using a pump (the safer method), connect the suction to the eduction pipe. If air pressure on the tank is required to prime and start pumping, it must be limited to 207 kPa (30 psi) maximum (MCA 1961).

4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles. The unloading of nitric acid tank trailers is similar to that of railway tank cars. The general procedures for tank cars apply equally well to tank trailers.

4.2.3 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading and handling system components discussed in this section not only include those materials generally used in nitric acid service, but also other materials that may be used for similar or particular application and materials that may be used in fuming nitric acid service. All materials discussed in this section appear in Table 7. The components of typical off-loading or handling systems that will be included are pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks. Even though some of the materials listed may be of a more exotic nature, it is felt advisable to present the most comprehensive listing that can be derived from the literature reviewed so as to give the handler the maximum options.

Suitable for use in piping are 316 or 316 L stainless steels; however, 304 L is slightly better than the former (CE 1980c). High silicon cast iron (Duriron, Durichlor 51 and Superchlor) is also used successfully for nitric acid. These materials are not attacked by all concentrations of nitric acid at normal temperatures. Boiling nitric acid at concentrations above 50 percent has no effect on high silicon iron although weak solutions will attack the material slightly (Durco 1979). Figure 9 shows the resistance of Duriron to nitric acid at various concentrations versus temperature. High silicon iron is in cast form only and has limited shock resistance.

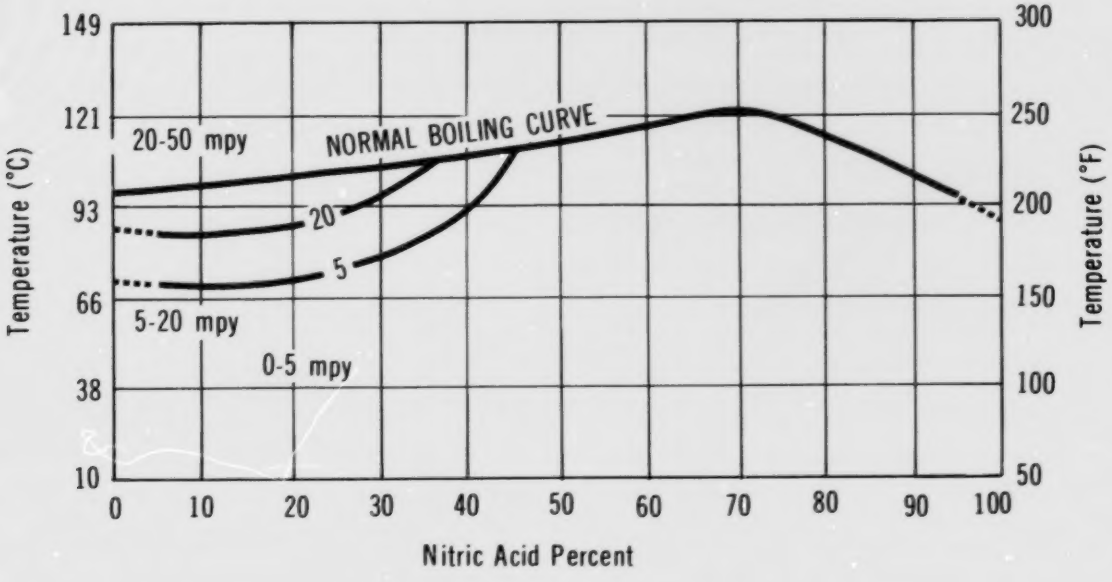
As is the case with all unloading/handling operations, the size of the pipe and coupling device must be compatible with the tank car/equipment to which coupling must be afforded. Normal process pipe may be almost any size; however, pipe under 25 mm (1 in.) is not recommended. Outdoor lines should be self-draining. Swivel joints

FIGURE 9

NITRIC ACID

RESISTANCE OF DURIRON TO NITRIC ACID

Reference: DURCO 1979



may be used for flexible sections. Either the ball-bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance (MWPP 1978).

Stainless steel is commonly used for storage containers for nitric acid less than 99 percent by weight; aluminum is used for concentrations over 99 percent. The latter should not be used for concentrations below 85 percent (MCA 1961; CE 1980b). Refer to Table 6 for other specifics.

Aluminum (various grades) and stainless steel (various grades) are approved for use with fuming nitric acids at room temperature. Most other materials, ferrous and nonferrous, react with the fuming acid to produce oxides of nitrogen. Titanium must be particularly avoided with red fuming nitric acid as ignition may occur if the water content is below 1.5 percent and the nitrogen dioxide content is above 2.5 percent (CPIA 1970; CE 1980b; AFRPL 1977). Specifics on other metals are shown in Table 6. Other materials approved for use with the fuming acids are the nonmetals Kel-F-81, TFE, Halon TFE and Resin X Epoxy, and lubricants Nordcoseal-147-5, Fluorolube and perfluorocarbos (CPIA 1970).

Piping and fittings for use with the fuming nitric acids should be of approved material, aluminum or stainless steel, and tested at design pressure. Welding should be used as an installation technique. Valves of the plug type are most satisfactory; gate valves are not recommended. Valves should be constructed of approved materials. Gasket materials recommended are sheet TFE (Halon TFE or Teflon), Kel-F (chlorotrifluoroethylene polymer), aluminum (approved grade), Teflon-sheathed asbestos (envelope) or corrugated aluminum with asbestos-filled depressions (Note: asbestos material should be used with caution). Pumps should be constructed of approved materials and may be of a centrifugal or positive-displacement type. The shaft seal should be either a mechanical seal constructed of fuming acid-resistant material, or of braided blue asbestos packing impregnated with approved lubricant. Acid hoses should be made of flexible braided-stainless steel wire with TFE or stainless steel bellows inner liner. Storage containers should be of welded construction and stress relieved. Aluminum is the usual material of construction and the tank is of the horizontal type. Stainless steel containers are subject to corrosion failure at the welded areas due to carbide precipitation that takes place during the welding process. Proper heat treatment after fabrication will reduce this danger significantly. User manuals provided by manufacturers should be consulted for specific details regarding handling equipment, equipment design, and facility design (CPIA 1970). This manual provides cursory data thought suitable for use in emergency situations.

4.3 Compatibility with Materials of Construction

The compatibility of nitric acid with materials of construction is indicated in Table 6. The unbracketed abbreviations are described in Table 7. The rating system for this report is briefly described below.

Recommended:	This material will perform satisfactorily in the given application.
Conditional:	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
Not Recommended:	Material will be severely affected in this application and should not be used.

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	5-50%	21 to boiling	SS 304, 304L, 316, 316L (SFC 1982; GAC)		
	<10%	24	ABS (MWPP 1978)	Inconel (SFC 1982)	Monel (SFC 1982)
		To operating limit of material	PVC I PE (MWPP 1978)		
	10%	66	PVDC (DCRG 1978)		
		79	Chlorinated Polyether PP (DCRG 1978)		
		93	PVDF (DCRG 1978)		
	To 20%	≤66	Duriron (Durco 1979)		
	20%	23	PVC I (DPPED 1967)	PVC II (DPPED 1967)	ABS (DPPED 1967)
		49	PE (DPPED 1967)		
		60			PVC I PVC II (DPPED 1967)
	30%	52	PP (CE 1980b)		
	40%	60	PVC (CE 1980b)		
	>45%	>71	High Silicon Iron (CE 1980b)		
	<50%	To operating limit of material	PVC I PE (MWPP 1978)		
					ABS (MWPP 1978)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)	50%	24	Chlorinated Polyether (DCRG 1978)		
		52	PVDC (DCRG 1978)		
		66	PP (DCRG 1978)		
		79	PVDF (DCRG 1978)		
	>50%	Boiling	Duriron, Durichlor 51, Superchlor (Durco 1979)		
	60%	23	PVC I (DPPED 1967)	PVC II (DPPED 1967)	
		25	PP PVC (CE 1980b)		
		60			PVC I PVC II (DPPED 1967)
	65%	Boiling	SS 304, 316 (GAC) Nitronic 50		
	68%	23		PVC I (DPPED 1967)	PVC II (DPPED 1967)
		60			PVC I PVC II (DPPED 1967)
	70%	24	Chlorinated Polyether PP, PVDC (DCRG 1978) PE (MWPP 1978)		
		To operating limit of material	PVC I* (MWPP 1978)		
			ABS (MWPP 1978)		

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)	Conc.	21	SS 304, 304L, 321, 347, 316, 316L, Inconel (SFC 1982)		Ni, Monel (SFC 1982)
	Conc.	Boiling			SS 304, 304L, 321, 347, 316, 316L Ni, Monel, Inconel (SFC 1982)
		To boiling or temperature limit or material	TFE, FEP (CE 1980b)		Furan Resin, Phenolic Resin, Epoxy Resin NR (hard) (CE 1980b)
	All conc.	RT	Duriron, Durichlor 51, Superchlor (Durco 1979)		
	Fuming	-	Duriron, Durichlor 51, Superchlor (Durco 1979)		
2. Valves	All	21	"20" Alloy SS 316 (JSSV 1979)		
		5-70%	Cer-Vit (Schott)		
	Up to 65%	Boiling	SS 316 (JSSV 1979)		
	Conc.	Boiling	Alloy 20 (CE 1983b)		
3. Pumps	20%	49	GRP with FPM "0" Ring		
	Conc.	Boiling	SS 446 High Silicon Cast Iron (HIS 1969) TFE (CE 1980b)		

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Pumps (Cont'd)	Dilute		SS 410 SS 446		
	5-50%	Boiling	SS 304 SS 316 (GAC)		
	To 20%	≤66	High Silicon (Durco 1979)		
	>45%	>71	Cast Iron (HIS 1969; CE 1980b)		
4. Storage	60.4		SS (Du Pont MSDS 1980)		
	≤99		SS (MCA 1961)		
	>99		Aluminum (MCA 1961)		
	>95 or <85		Aluminum 3003, 5052 (CE 1980b)		
	WFNA, RFNA	27	Aluminum 1060, 1100, 3003, 3004, 6061, 5052, 5154 SS 301, 302, 303, 304, 309, 310, 316, 318, 321, 322, 347 Durimet 20 (AFRPL 1977; CPIA 1970)		
	WFNA, RFNA	49			SS 316 (AFRPL 1977)
5. Others	5%	20	SS 302 321, 347 (SFC 1982) SS 410 SS 430 (ASS)		
	5%	25	Ta, Nb, Zr, Ti, Hastelloy C-276 Alloy 20 (CE 1983b)		Hastelloy B-2, Monel 400 (CE 1983b)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	10%	60	PVC (TPS 1978)		
		21	FPM (CE 1980a)	IIR, CSM Gatron (CE 1980a)	NR, CR, NBR, Tufflex, Polyelastomers, Nylon (CE 1980a) Brass, CS
	10%	82	PP (TPS 1978)		
		85	CPVC (TPS 1978) Graphite (CE 1980b)		
				Si (GPP)	SBR (GPP)
	10-20-40-69.5%	35	Zr, Ti, TiPd (AMC)		
		100	Ti, Zr, Ta, TiPd (AMC)		
	20%	60	Graphite, impervious (CE 1980b)		
	20% (aerated)	290		Ti (AMC)	
	25%	21	FPM (CE 1980a)	NR, IIR, CSM, Gatron, SS 304, SS 316 (CE 1980a)	CR, NBR, NBR + Plastic, NBR Mesh, Tufflex, Epichlorohydrin, Polyesterelastomer, Nylon (CE 1980a) CS, Brass
	10-30%	35	Ti, Zr (AMC)		
	Up to 30%	50	uPVC PE, PP IIR, EPDM FPM, CSM (GF)	CR (GF)	POM NR NBR (GF)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	40%	21	FPM (CE 1980a)	Gatron SS 304, 316 (CE 1980a)	NR, IIR, EPDM, CSM, CR, NBR, NBR + Plastic, NBR Mesh, Tufflex, Epichlorohydrin, Polyesterelastomer, Nylon (CE 1980a) Brass, CS
		200	Zr (AMC)	TI (AMC)	
	48%	80		CR FPM (GF)	UPVC PE, PP POM, NR NBR, IIR EPDM CSM (GF)
	5-50%	21 to boiling			Ti, Pd (SFC 1982)
	50%	210	SS 302, 410 430 (ASS)		
		22	PVC CPVC (TPS 1978)		
		23	PP (TPS 1978)		
		49			PP (TPS 1978)
		85			CPVC (TPS 1978)
	60%	21		Gatron, FPM SS 304, 316 (CE 1980a)	NR, IIR, CSM, CR, NBR, Tufflex, Epichlorohydrin, Polyesterelastomer, Nylon, CS, Brass (CE 1980a)
	65%	Boiling	SS 316L, 317, 317L (Armco 1981b)	SS 302, 430 (ASS)	SS 410 (ASS)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)		66	Alloy 12, Alloy 21 (CE 1983a)		Alloy 6, Alloy 50, Alloy 60, Alloy 1, Ni-17, Cr-17 Mo-6, Fe-5W (CE 1983a)
	65% (aerated)	175	Ti, Zr, TiPd (AMC)		
	Conc.	Temperature line limit		Carbon Impregnated with Furan Carbon Impregnated with Phenolics (CE 1980b)	
		<65		Alloy C (CE 1980b)	
		≤boiling	Glass/silicates (CE 1980b)		
		boiling	Ta, Nb, Zr, Ti, Alloy 20 (CE 1983b)		Hastelloy C-276, B-2, SS 316 (CE 1983b)
	5-69.5%	100	Ti, Zr (AMC)		
	70%	22	PVC, CPVC (TPS 1978)		
		23		PP (TPS 1978)	
		49			PP (TPS 1978)
		60	PVC (TPS 1978)	uPVC CR* (GF)	PE, PP POM, NR NBR, IIR EPDM, FPM CSM (GF)
		85			CPVC (TPS 1978)
			CSM* (GPP)		SBR, CR Si (GPP)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	10 to 70%	24 to 204	Glass (CDS 1967)		
	80 to 100%	24 to 100	Glass (CDS 1967)		
	90-98%	25	Cer-Vit (Schott)		
	>95% (generally not for <85%)	-	Aluminum 3003, 5052		
	98% (aerated)	27	Ti, Zr (AMC)		
	98% (non-aerated)	R.T.	Ti (AMC)		
	100%	52	PVDF (CE 1980b)		
		Temperature limit of material	FEP, TEF (CE 1980b)		
	10 to 100%	24			Concrete (CDS 1967)
	10 to 30%	24			Wood (CDS 1967)
	WFNA (liquid or vapour)	RT	Ti (AMC)		
	WFNA (90%)	82		Ti (AMC)	
	WFNA	122		Ti (AMC)	
		160		Ti (AMC)	
	RFNA	RT			Ti (AMC)[1]
		21		FPM, SS 304, 316, Al (CE 1980a)	NR, IIR, EPDM, CSM, CR, NBR, NBR + Plastic, NBR Mud, Tufflex,

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)					Gatron, Epichlorohydrin, Polyesterelastomer, Nylon, CS, Brass (CE 1980a)
		23.9	Cast iron, (AFRPL 1977) Duriron, Ni-resist, Hastelloy C	Mild steel (AFRPL 1977)	Hastelloy B, Monel (AFRPL 1977)
		23.9-54		Inconel (AFRPL 1977)	
		27	Alloy 20, Durimet, Cr, Au (AFRPL 1977)		
		49			SS 316 (AFRPL 1977)
	RFNA	149	Pt (AFRPL 1977)		

* This material has been given a lower rating in a similar application by another reference.

1. NOTE: May ignite if water is less than 1.5 percent and nitrogen dioxide greater than 2.5 percent (CE 1980b)

TABLE 7 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
Au	Gold
	Alloy C (Ni-Cr-Mo)
	Alloy 12 (Cobalt-based)
	Alloy 21 (Cobalt-based)

TABLE 7 MATERIALS OF CONSTRUCTION (Cont'd)

Abbreviation	Material of Construction
	Alloy 6 (Cobalt-based)
	Alloy 50 (Nickel-based)
	Alloy 60 (Nickel-based)
	Alloy 1 (Cobalt-based)
	Alloy 20 (Stainless Steel with High Nickel)
	Aluminum
	Carbon
	Cast Iron, High Silicon
	Cer-Vit (Glass/Ceramic)
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
Cr	Chromium
CS	Carbon Steel or Iron
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Duriron (High Si Iron)
	Durichlor 51
	Durimet
	Durimet 20
EPDM	Ethylene Propylene Rubber
	Epoxy Resin
FEP	Teflon Polymer
FPM	Fluorine Rubber (Viton)
	Furan Resin
	Glass
GRP	Glass Reinforced Vinyl Ester
	Graphite
	Hastelloy C-276 (Ni-Cr-Mo)
	Hastelloy B-2 (Ni-Cu)
	Hastelloy B
	Hastelloy C

TABLE 7 MATERIALS OF CONSTRUCTION (Cont'd)

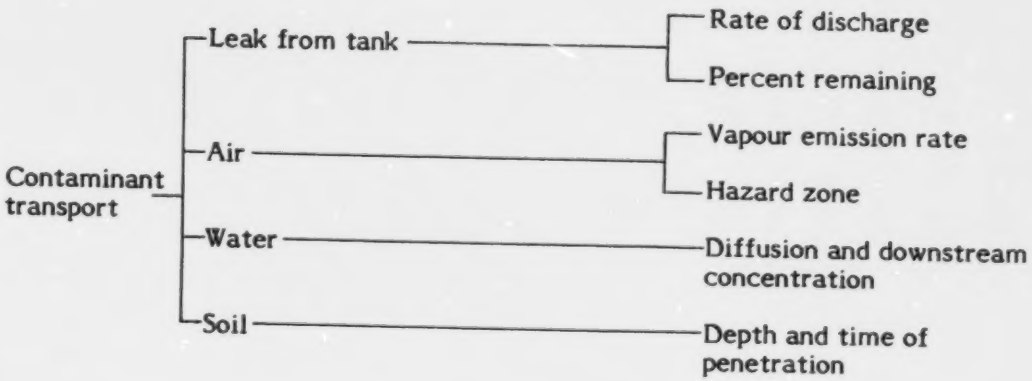
Abbreviation	Material of Construction
	Inconel
IIR	Isobutylene/Isoprene (Butyl) Rubber
	Niobium
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
	Nitronic 50 (Stainless Steel)
	Nitronic 60
NR	Natural Rubber
	Ni-resist
	Nickel
	Nickel-Copper Alloy (Monel)
	Phenolic Resin
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
Pt	Platinum
PVC (followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
Si	Silicon
SS (followed by grade)	Stainless Steel
	Superchlor
Ta	Tantalum
TFE	Teflon
Ti	Titanium
TiPd	Titanium/Palladium Alloy
uPVC	Unplasticized Polyvinyl Chloride
	Wood
Zr	Zirconium

5 CONTAMINANT TRANSPORT

5.1 General Summary

Nitric acid spills will release vapours to the atmosphere. Because nitric acid is denser than water and miscible with it, spills in water will sink and mix as well as produce vapour. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may be an environmental concern.

The following factors are considered for the transport of a spill in water and soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Nitric acid is occasionally transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of

about 80 000 L. It is noted here that the most typical capacity for a nitric acid car is 30 300 L; however, for consistency the standard noted above will be used.

If a tank car loaded with nitric acid is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of nitric acid and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

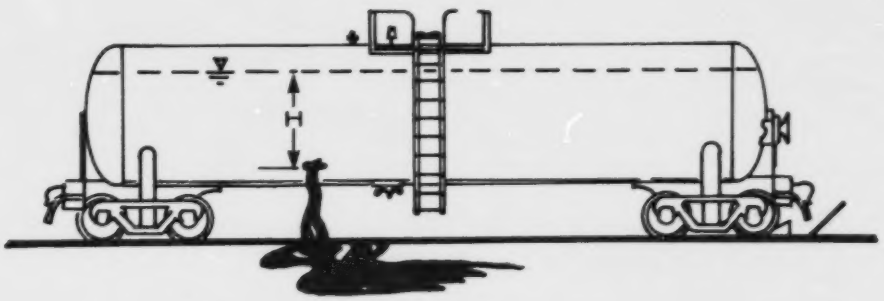


FIGURE 10 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of nitric acid. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 12: Discharge rate versus time. Figure 12 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only directly

FIGURE 11

NITRIC ACID (42°Bé)

PERCENT REMAINING VS TIME

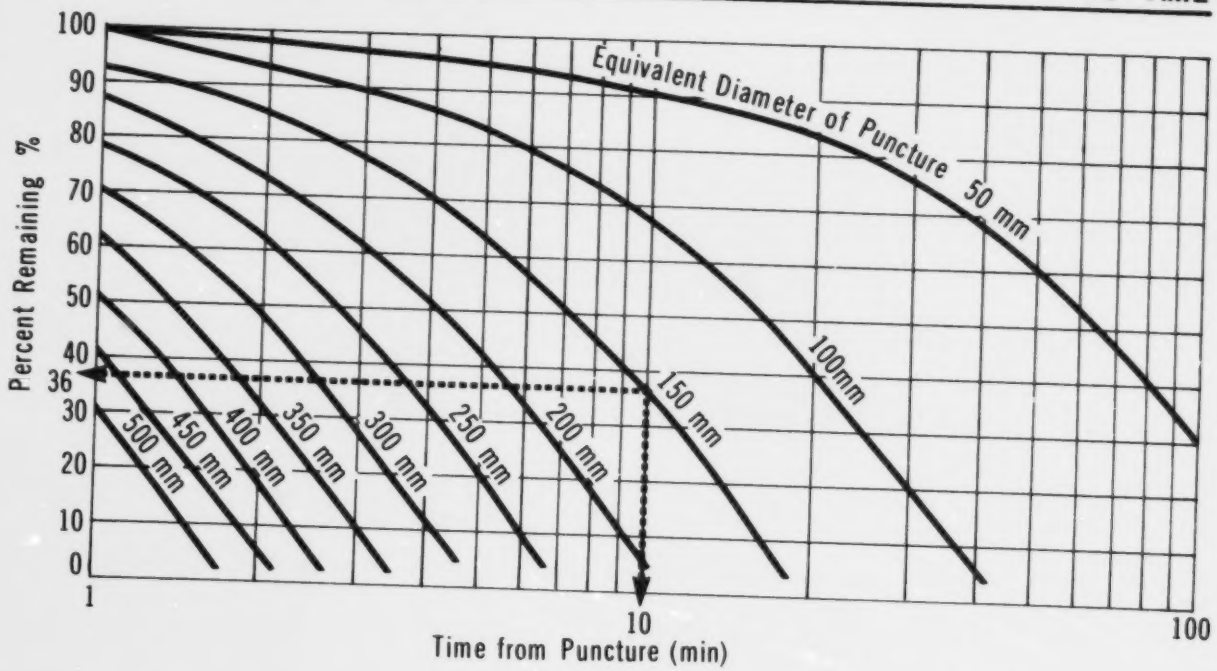
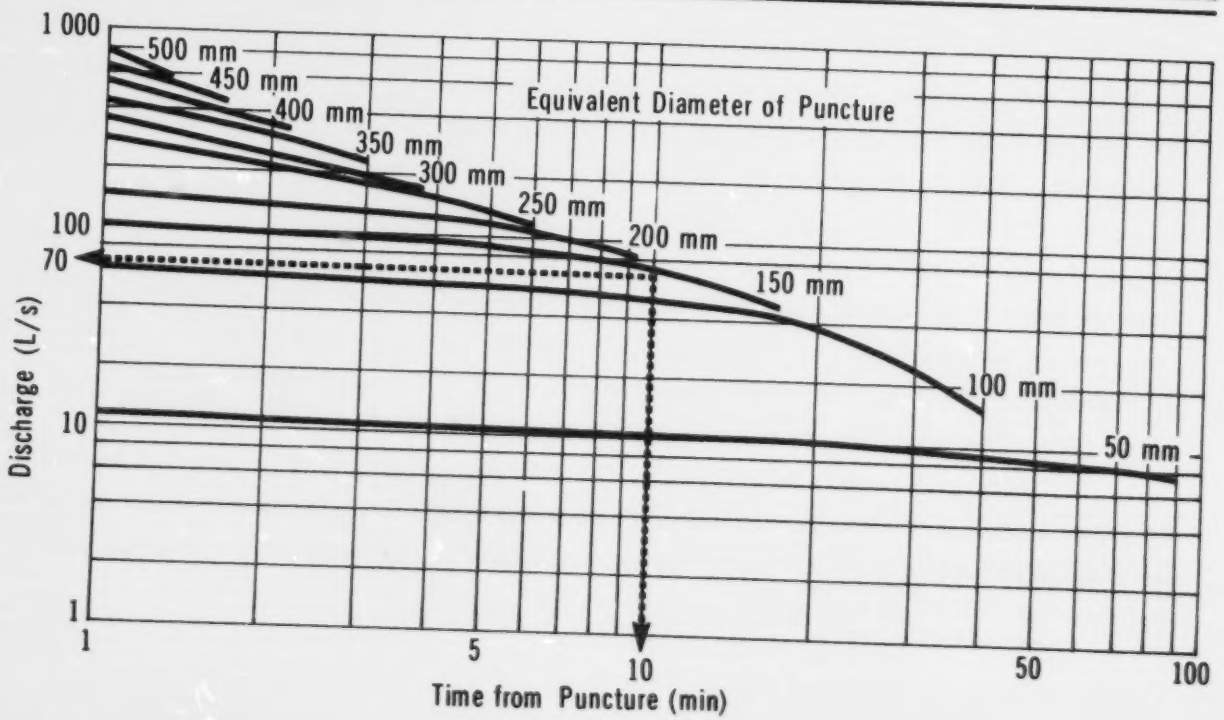


FIGURE 12

NITRIC ACID (42°Bé)

DISCHARGE RATE VS TIME



applicable to the standard tank car size with an initial volume of 80 000 L. A worst case approximation will be obtained if applied to a 30 300 L tank car.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with nitric acid has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 11
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the incident?

Solution to Problem B

- Use Figure 12
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since nitric acid has a relatively low volatility, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

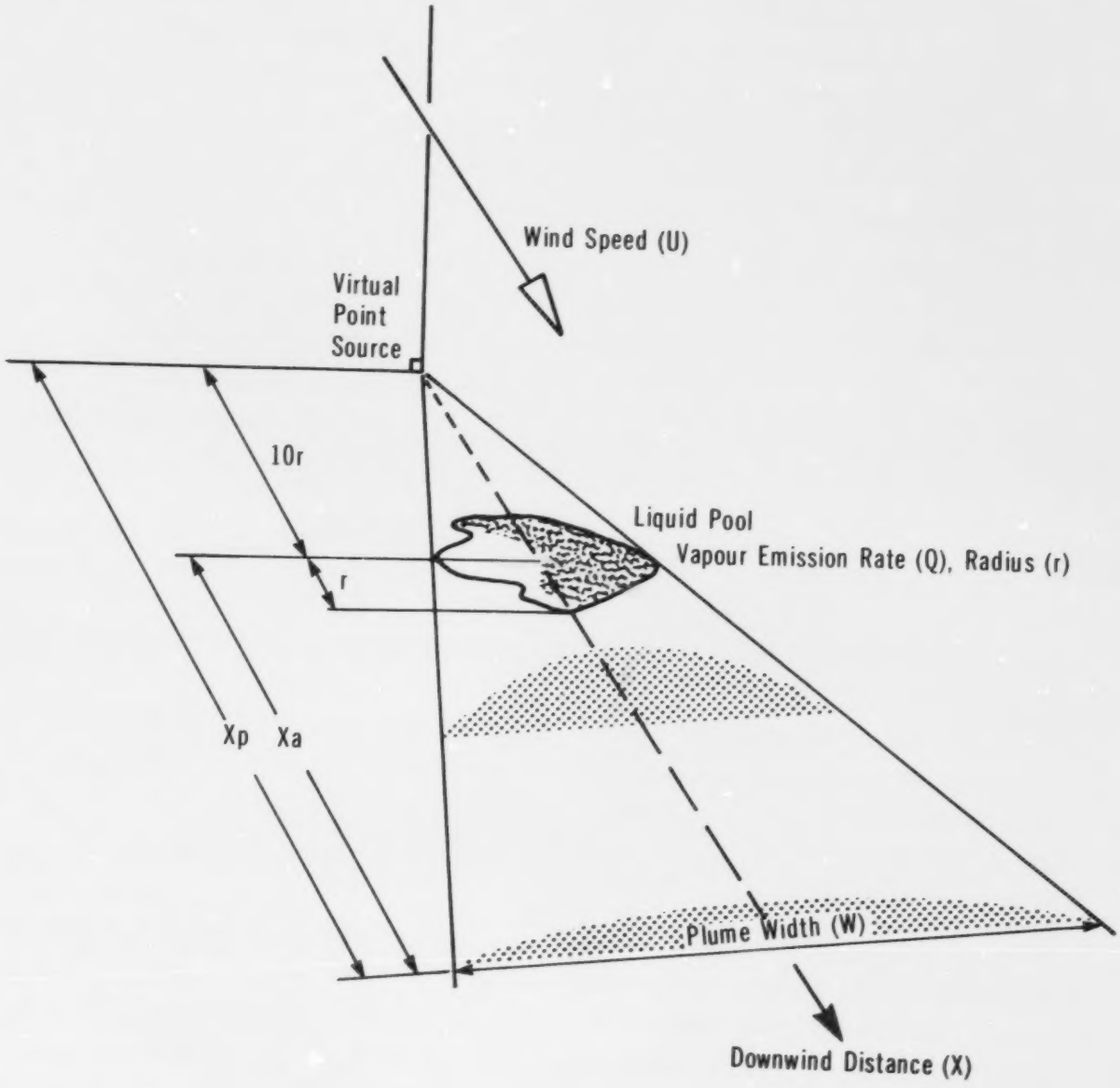
To estimate the vapour concentrations downwind of the accident site for the determination of the toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 13 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

FIGURE 13

NITRIC ACID

SCHEMATIC OF CONTAMINANT PLUME



It should be noted that the vapours released from a spill of nitric acid (≈70 percent by weight) have been assumed to be composed entirely of nitric acid. The exact composition of the vapour produced from a pool of nitric acid depends on such factors as ambient temperature, relative humidity and what material comes into contact with the acid. Depending upon these factors, the vapour may consist of a mixture of nitric acid and various oxides of nitrogen, particularly NO_2 (Sax 1981). Since nitric acid has a lower TLV• than, for example, NO_2, conservative results will be obtained here by assuming all vapour is emitted as nitric acid vapour.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Figure 15:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 8:	weather conditions
Figure 16:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 9:	maximum plume hazard half-widths
Figure 18:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 14 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 15: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for nitric acid (as 70 percent by weight in aqueous solution) has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for nitric acid at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.069 g/(m^2s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which at a given speed is dependent on ambient temperature and the vapour pressure (Perry 1973) of nitric acid at that temperature. For example, evaporation rates of 0.02 g/(m^2s) at 0°C and 0.12 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s. Note that in an actual spill

FIGURE 14

NITRIC ACID

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

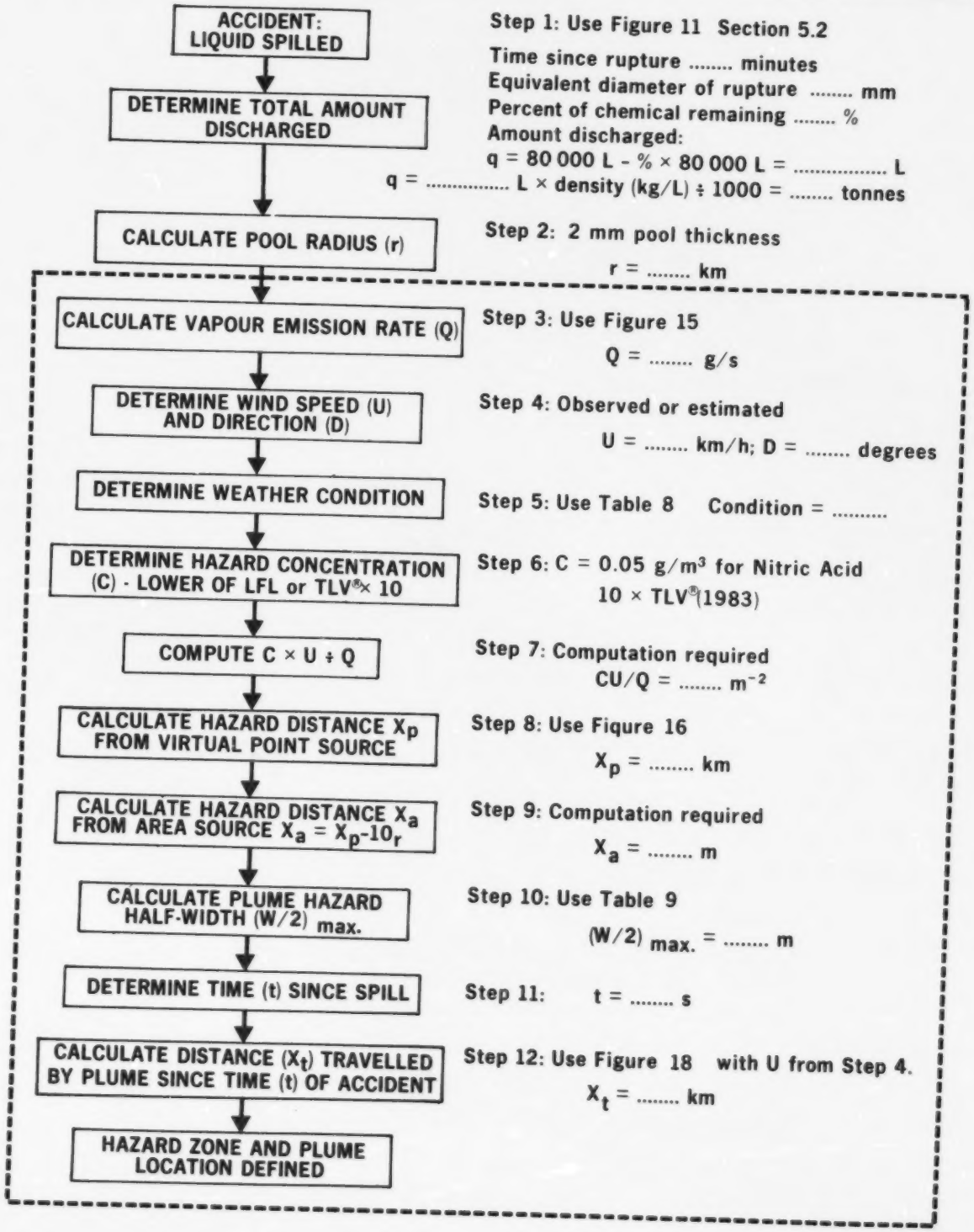
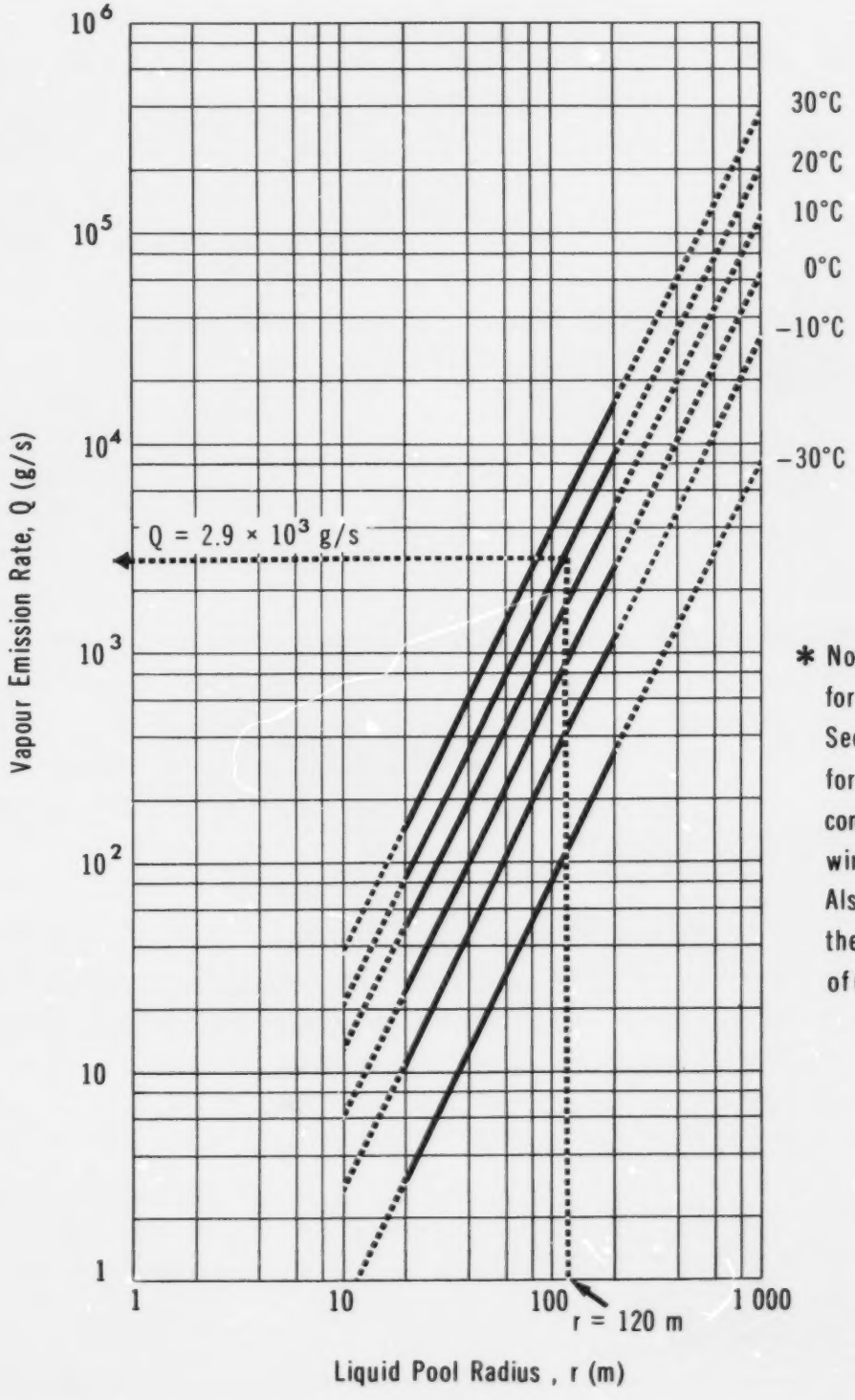

ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
CALCULATE POOL RADIUS (r)
CALCULATE VAPOUR EMISSION RATE (Q)
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C × U ÷ Q
CALCULATE HAZARD DISTANCE Xp FROM VIRTUAL POINT SOURCE
CALCULATE HAZARD DISTANCE Xa FROM AREA SOURCE Xa = Xp-10r
CALCULATE PLUME HAZARD HALF-WIDTH (W/2) max.
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (Xt) TRAVELLED BY PLUME SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PLUME LOCATION DEFINED
Step 1: Use Figure 11 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80 000 L - % × 80 000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes
Step 2: 2 mm pool thickness
r = ... km
Step 3: Use Figure 15
Q = ... g/s
Step 4: Observed or estimated
U = ... km/h; D = ... degrees
Step 5: Use Table 8 Condition = ...
Step 6: C = 0.05 g/m³ for Nitric Acid
10 × TLV®(1983)
Step 7: Computation required
CU/Q = ... m⁻²
Step 8: Use Fiqure 16
Xp = ... km
Step 9: Computation required
Xa = ... m
Step 10: Use Table 9
(W/2) max. = ... m
Step 11: t = ... s
Step 12: Use Figure 18 with U from Step 4.
Xt = ... km

FIGURE 15

NITRIC ACID (42°Bé)

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.05 to 120 tonnes.

situation, nitric acid vapour released from the liquid pool will lower the concentration in the liquid phase and result in lower nitric acid evaporation rates with time. The use of the value at the initial nitric acid concentration will therefore be the worst case situation.

Use: For a pool of nitric acid of known radius, the rate (Q) at which nitric acid vapour is released to the atmosphere at a given temperature can then be estimated from Figure 15. The solid portions of the curves represent spills of 0.05 to 112 tonnes, the latter representing about one standard 80 000 L rail car load of nitric acid. It should be noted that Figure 15 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of nitric acid vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was arbitrarily chosen as an intermediate value between that of benzene (a moderately volatile liquid) and that of iso-amyl nitrite (a nonvolatile liquid). This model situation was chosen to apply for water-soluble liquids with boiling points above ambient temperature, and to a limited number of water-soluble and water-insoluble organic liquids that are not treated by CHRIS (CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 16: Normalized vapour concentration versus downwind distance. Figure 16 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 16, the weather condition must be determined from Table 8.

FIGURE 16

NITRIC ACID (42° Bé)

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

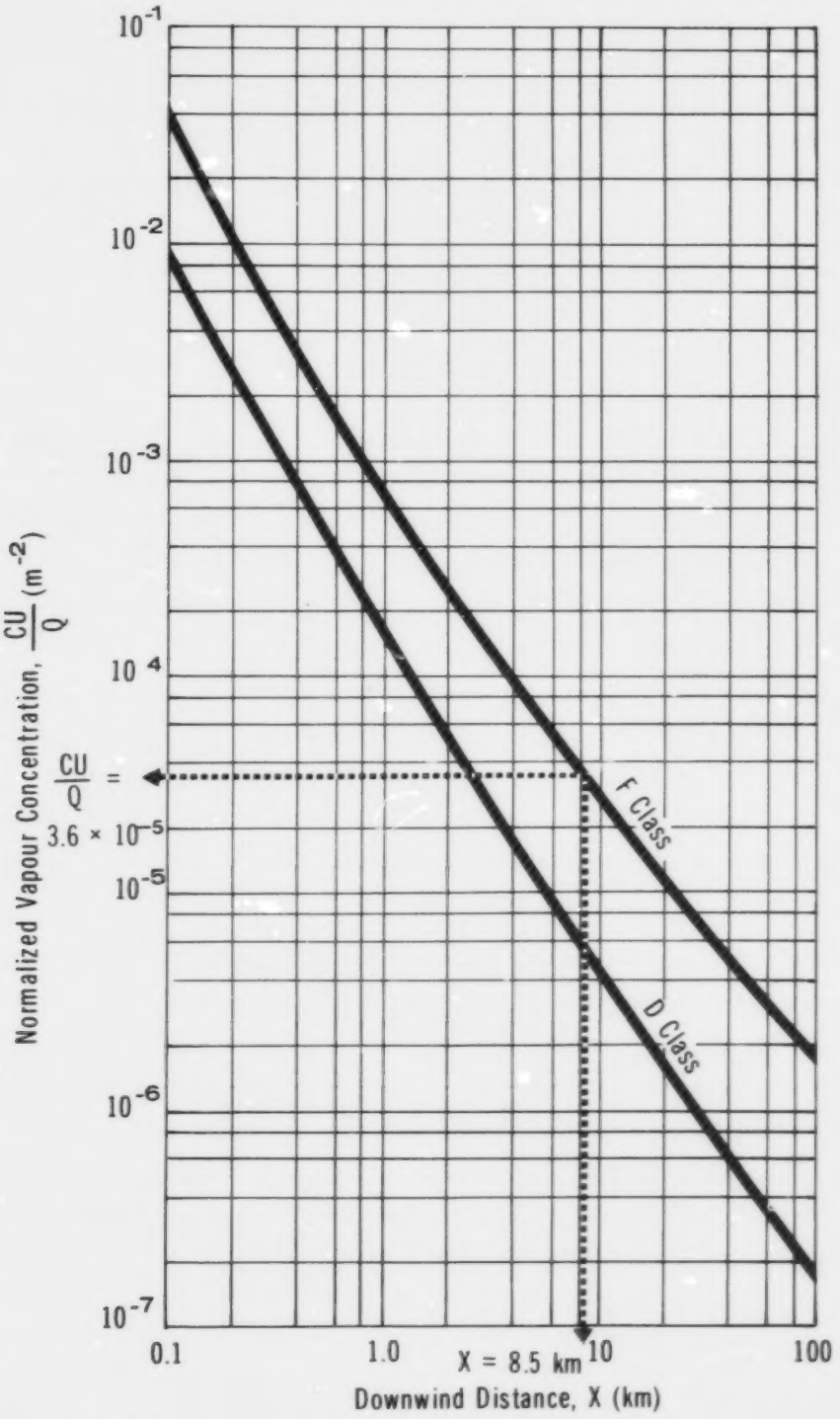


TABLE 8 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed < 11 km/h (≈ 3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 16 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3), which for an inflammable vapour will be 10 x TLV®. Note: To convert the TLV®, in ppm, to a concentration in g/m^3, use Figure 17

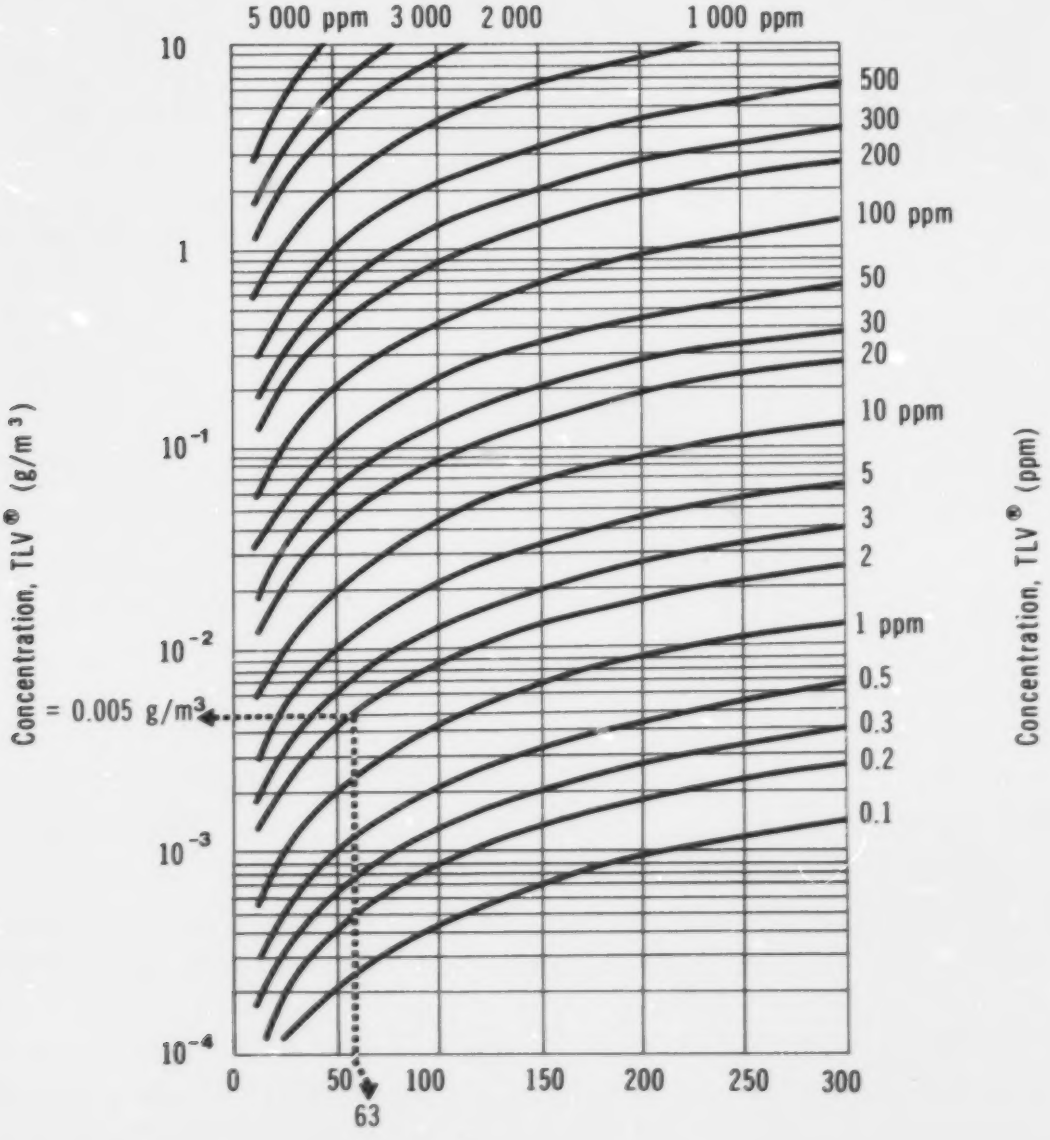
A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.3 **Table 9: Maximum plume hazard half-widths.** This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the nitric acid Threshold Limit Value (TLV®) of 0.005 g/m^3, or 0.05 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the nitric acid vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 9 is therefore only applicable for a nitric acid hazard concentration limit of 10 x TLV®, or 0.05 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

FIGURE 17

NITRIC ACID

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Example: Nitric Acid, MW = 63, TLV® = 2 ppm
then TLV® in g/m³ = 0.005

Note: data applicable at 25°C and 760 Hg pressure

TABLE 9 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR NITRIC ACID (42° Be) AT 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
350 000	3430	(99.5 km)*	30 000	1430	(99.5 km)*
300 000	3115		25 000	1250	
250 000	2785		20 000	1060	
200 000	2425		15 000	850	
175 000	2235		10 000	630	
150 000	2030		7 500	510	
125 000	1815		5 000	375	
100 000	1580		2 500	240	
75 000	1320	Q/U = 1380 →	1 500	175	→ $W/2_{max}$ = 175 m
50 000	1030		1 000	135	
30 000	750		750	110	
25 000	670		500	85	
20 000	585		250	55	
15 000	500		100	35	
10 000	395		50	25	
7 500	335				
5 000	260				
2 500	175				
1 000	100				
750	85				
500	70				
250	50				
100	30				
50	20				

* Data are provided up to a maximum downwind hazard distance of 100 km.

Example: A spill releasing nitric acid vapour at the rate of $Q = 2.9 \times 10^3$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 1380 g/m, which results in a maximum plume hazard half-width $(W/2)_{max}$ = 175 m.

Note: Above table is valid only for a nitric acid concentration of 10 x TLV•, or 0.05 g/m^3.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 1500 to 350 000 g/s, corresponding to nitric acid spills in the range of about 6 to greater than 6000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 120 000 kg, or approximately 120 tonnes. Therefore, under class D of Table 9, data are provided for up to about 50 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 150 to 30 000 g/s, corresponding to nitric

acid spills in the range of about 0.3 to 700 tonnes, respectively. Therefore, under class F of Table 9, data are provided for up to almost 6 times a standard rail car load.

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 9.

5.3.2.4 Figure 18: Plume travel time versus travel distance. Figure 18 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the plume has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid nitric acid. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of nitric acid were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution

Step 1: Quantity spilled is given, q = 20 tonnes

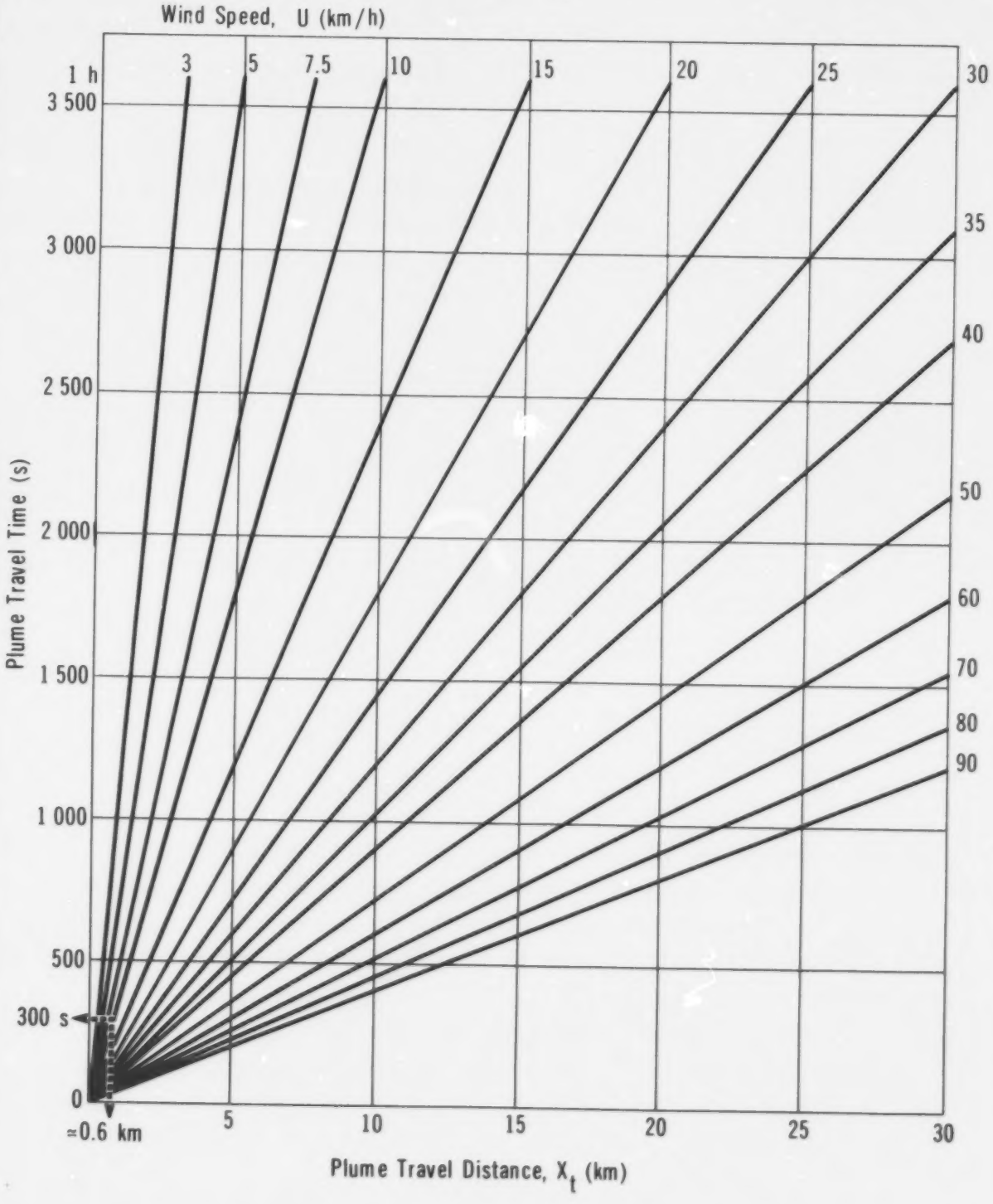
Step 2: Determine the pool radius (r) for a spill of 20 tonnes

- Use the observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 mm spill thickness
- Radius (r) = 120 m ÷ 1000 = 0.12 km

FIGURE 18

NITRIC ACID

PLUME TRAVEL TIME VS TRAVEL DISTANCE



Step 3: Calculate the vapour emission rate (Q) at T = 20°C

- From Figure 15, for r = 120 m and T = 20°C, Q = 2.9×10^3 g/s

Step 4: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:

  U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s

  D = NW or 315° (D = Direction from which wind is blowing)

Step 5: Determine the weather condition

- From Table 8, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL; since nitric acid vapours are not flammable, this is 10 x TLV®

  C = 0.05 g/m^3 (TLV® = 0.005 g/m^3; no LFL)

Step 7: Compute CU/Q

- $CU/Q = \dfrac{0.05 \times 2.1}{2.9 \times 10^3} = 3.6 \times 10^{-5}\ m^{-2}$

Step 8: Calculate the downwind distance (X_p) from the virtual point source

- From Figure 16 with CU/Q = 3.6×10^{-5} m^{-2} and weather condition F, $X_p \approx 8.5$ km

Step 9: Calculate the hazard distance (X_a) downwind of the area source

- With X_p = 8.5 km and r = 0.12 km then

  $X_a = X_p - 10\ r = 8.5\ km - 10\ (0.12\ km) = 7.3\ km$

Step 10: Calculate the plume hazard half-width $(W/2)_{max}$

- Use Table 9
- With Q = 2.9×10^3 g/s and U = 2.1 m/s

  then $Q/U = \dfrac{2.9 \times 10^3}{2.1} = 1380$ g/m

  Then for weather condition F the closest Q/U value is 1500 g/m which gives $(W/2)_{max} \approx 175$ m

Step 11: Determine the time since the spill

- $t = 5 \text{ min} \times 60 = 300 \text{ s}$

Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident

- Using Figure 18 with $t = 300$ s and $U = 7.5$ km/h, then $X_t = 0.6$ km (more accurately from $Ut = 2.1 \text{ m/s} \times 300 \text{ s} = 630 \text{ m} = 0.63 \text{ km}$)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (175 m) by the maximum hazard distance downwind of the area source (7.3 km) along the direction of the wind, as shown in Figure 19
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 20
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 53 minutes before the plume reaches the maximum downwind hazard distance of 7.3 km

5.4 Behaviour in Water

5.4.1 Introduction. As well as producing harmful concentrations of vapour, nitric acid will mix rapidly when spilled on a water surface. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion. To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d < 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

FIGURE 19

NITRIC ACID (42°Bé)

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

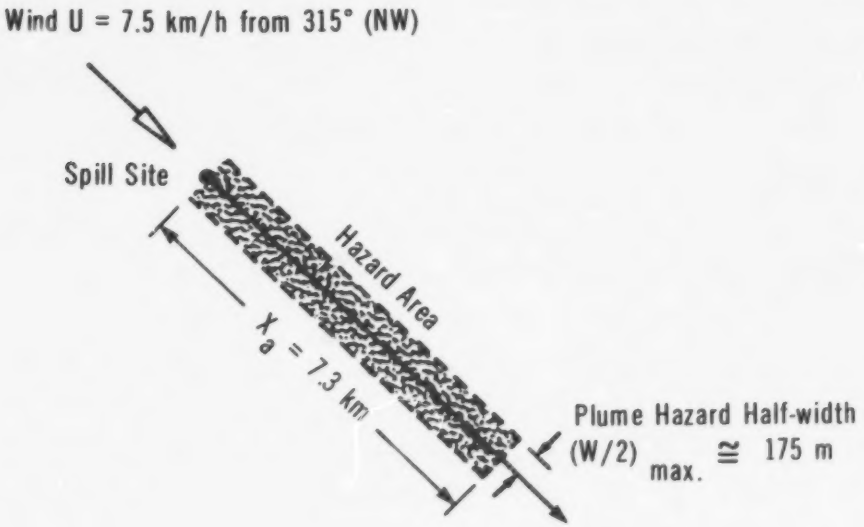
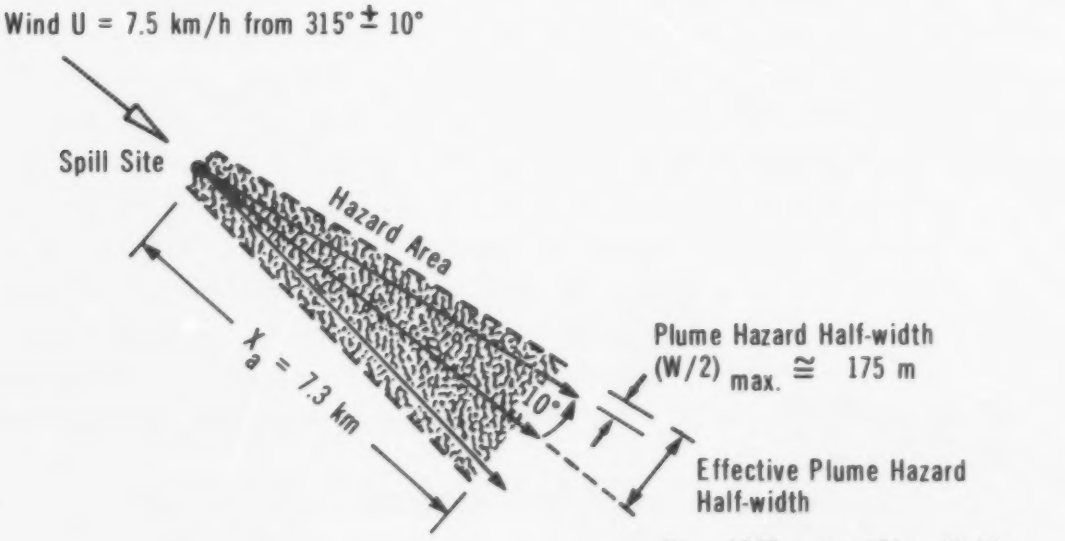


FIGURE 20

NITRIC ACID (42°Bé)

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X_a = 7.3 km
10°
Plume Hazard Half-width
$(W/2)_{max.} \cong$ 175 m
Effective Plume Hazard Half-width
= Xa × 1000 × tan 10° + $(W/2)_{max}$
= 7.3 × 1000 × 10° + 175 m
= 1460 m or 1.5 km

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate concentrations in non-tidal rivers and in lakes (still water).

Non-Tidal Rivers

Figure 22: time versus distance for a range of average stream velocities

Figure 23: hydraulic radius versus channel width for a range of stream depths

Figure 24: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 25: alpha* versus diffusion coefficient for various time intervals

Figure 26: alpha versus delta* for a range of spill sizes

Figure 27: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 28: volume versus radius for the hazard zone for a range of lake depths

Figure 29: average concentration versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 21 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 22 through 29) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 22: Time versus distance. Figure 22 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 22.

Figure 23: Hydraulic radius versus channel width. The model used to estimate the downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 23 is a

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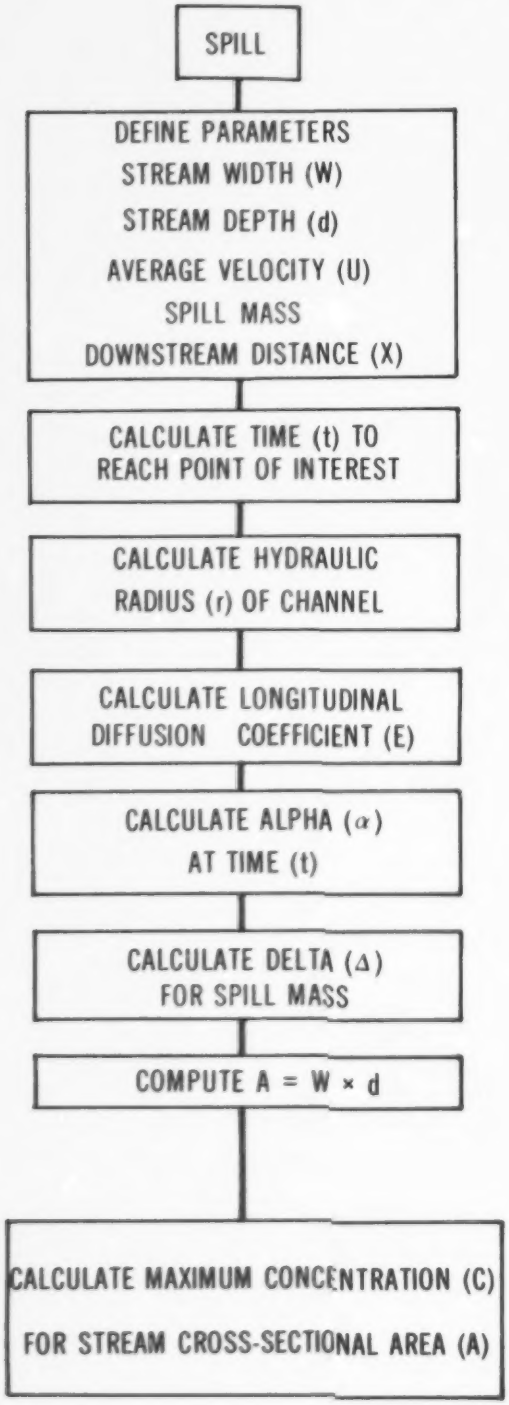
* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

FIGURE 21

NITRIC ACID

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 22

t = _____ minutes

Step 3: Use Figure 23

r = _____ m

Step 4: Use Figure 24

E = _____ m^2/s

Step 5: Use Figure 25

α = _____

Step 6: Use Figure 26

Δ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 27

C = _____ ppm

FIGURE 22

NITRIC ACID

TIME vs DISTANCE

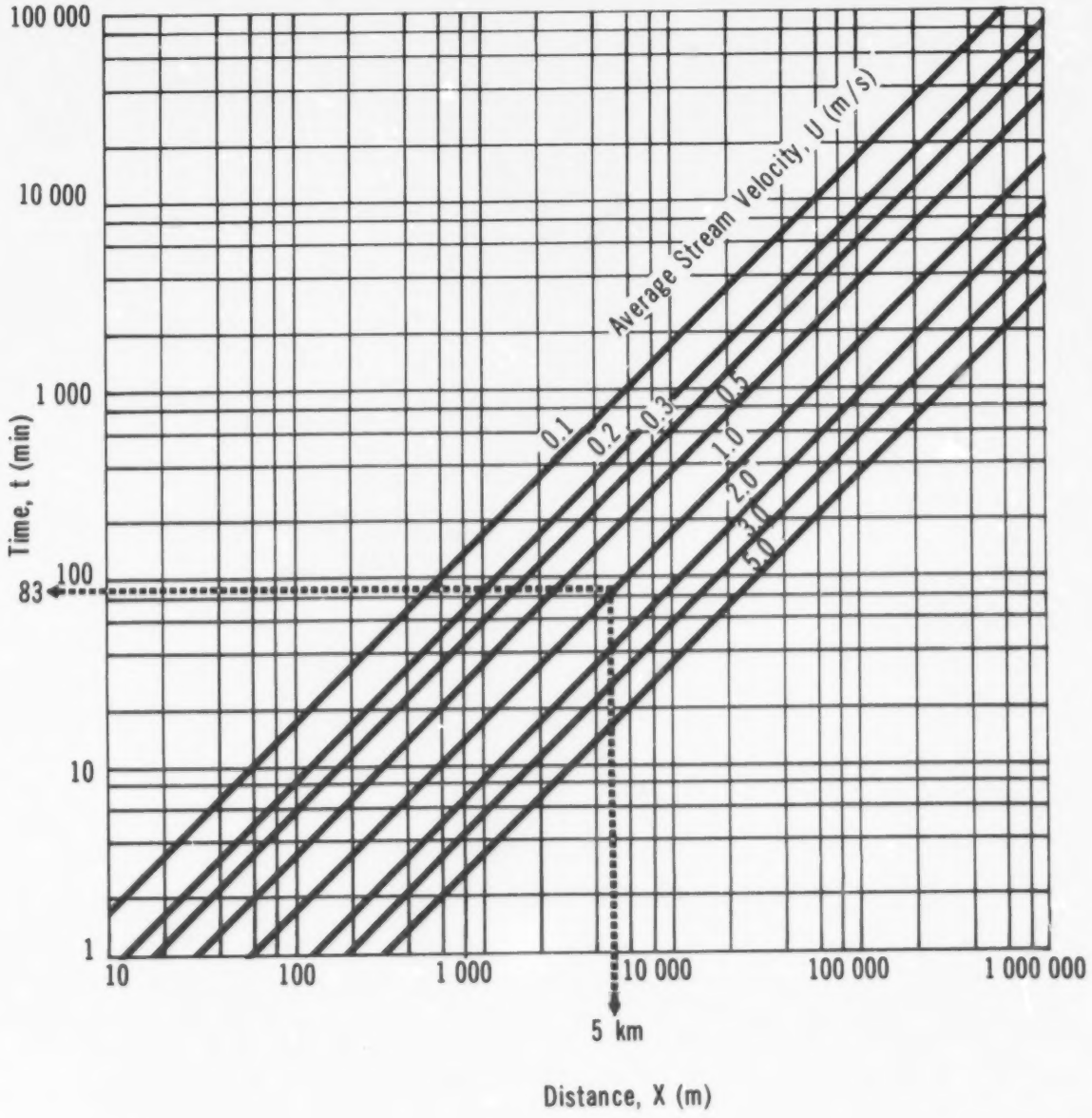
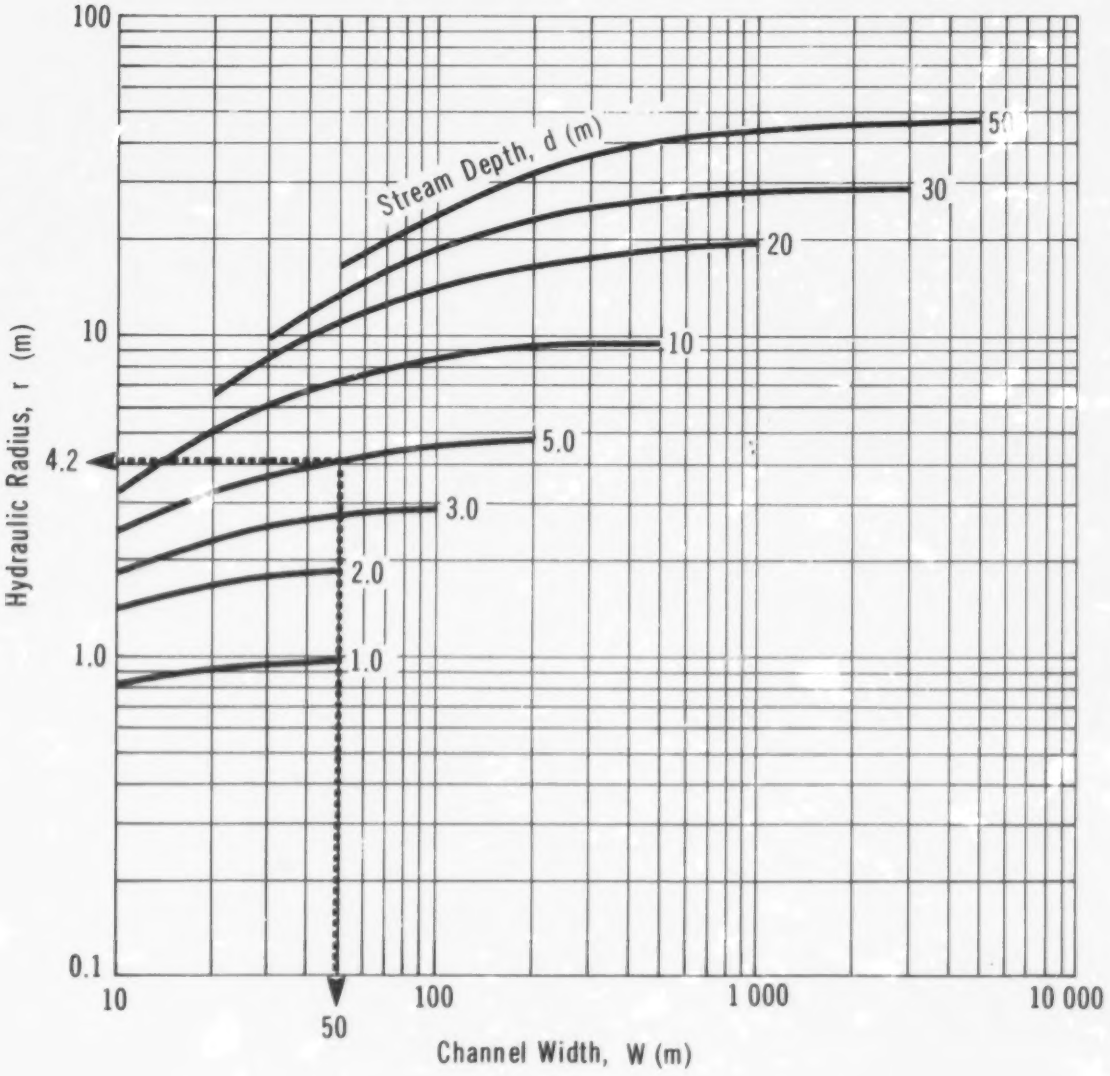


FIGURE 23

NITRIC ACID

HYDRAULIC RADIUS VS CHANNEL WIDTH



nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 24: Diffusion coefficient versus hydraulic radius. Figure 24 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 24 and the average stream velocity (U).

Figure 25: Alpha versus diffusion coefficient. Figure 25 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 26: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 26 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 27: Maximum concentration versus delta. Figure 27 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 27 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 28: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 28. The radius (r) represents the distance from the spill to the point of interest.

Figure 29: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 29 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of 50 percent nitric acid solution has occurred in a river. The stream width is 50 m and the stream

FIGURE 24

NITRIC ACID

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

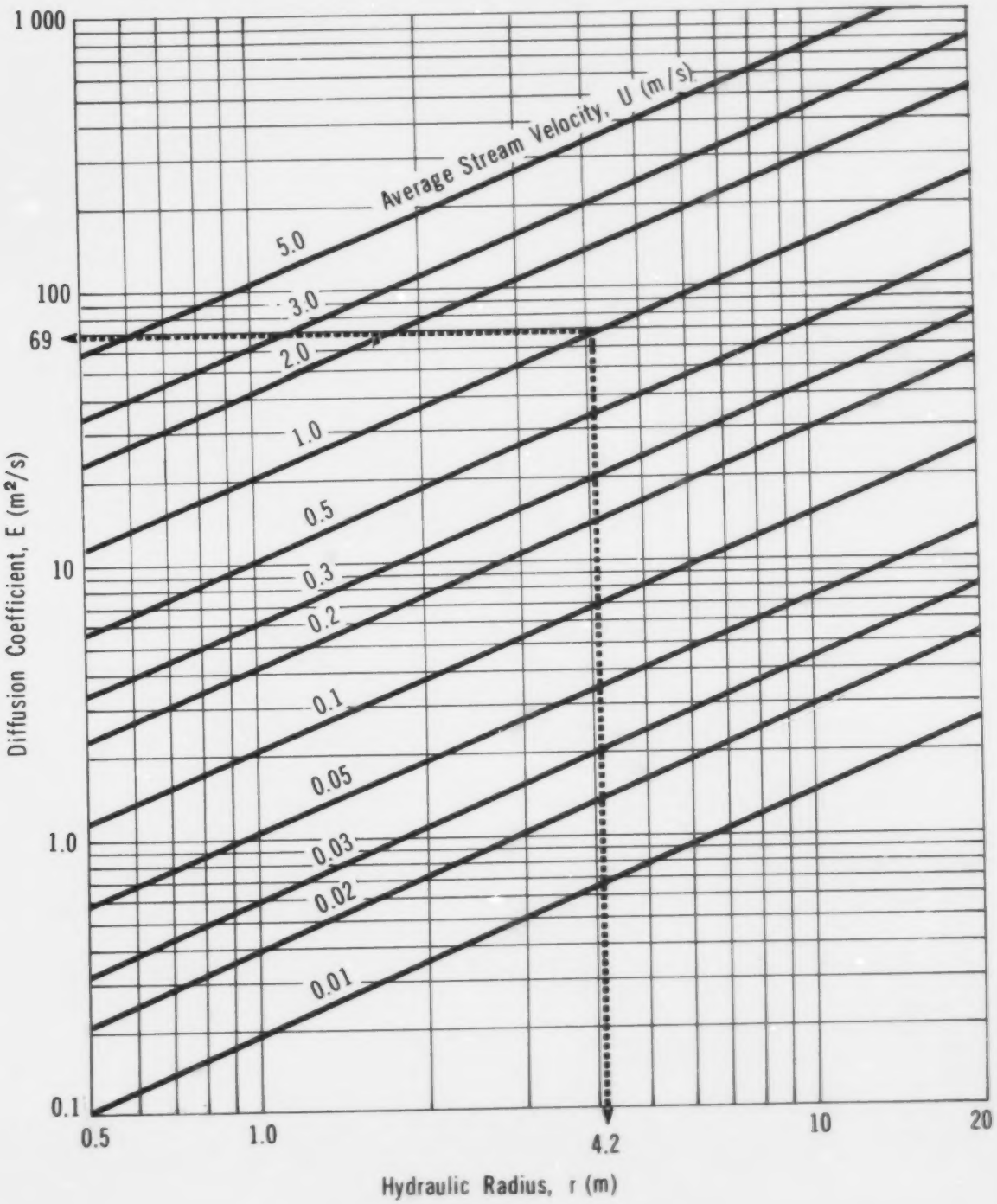


FIGURE 25

NITRIC ACID

ALPHA vs DIFFUSION COEFFICIENT

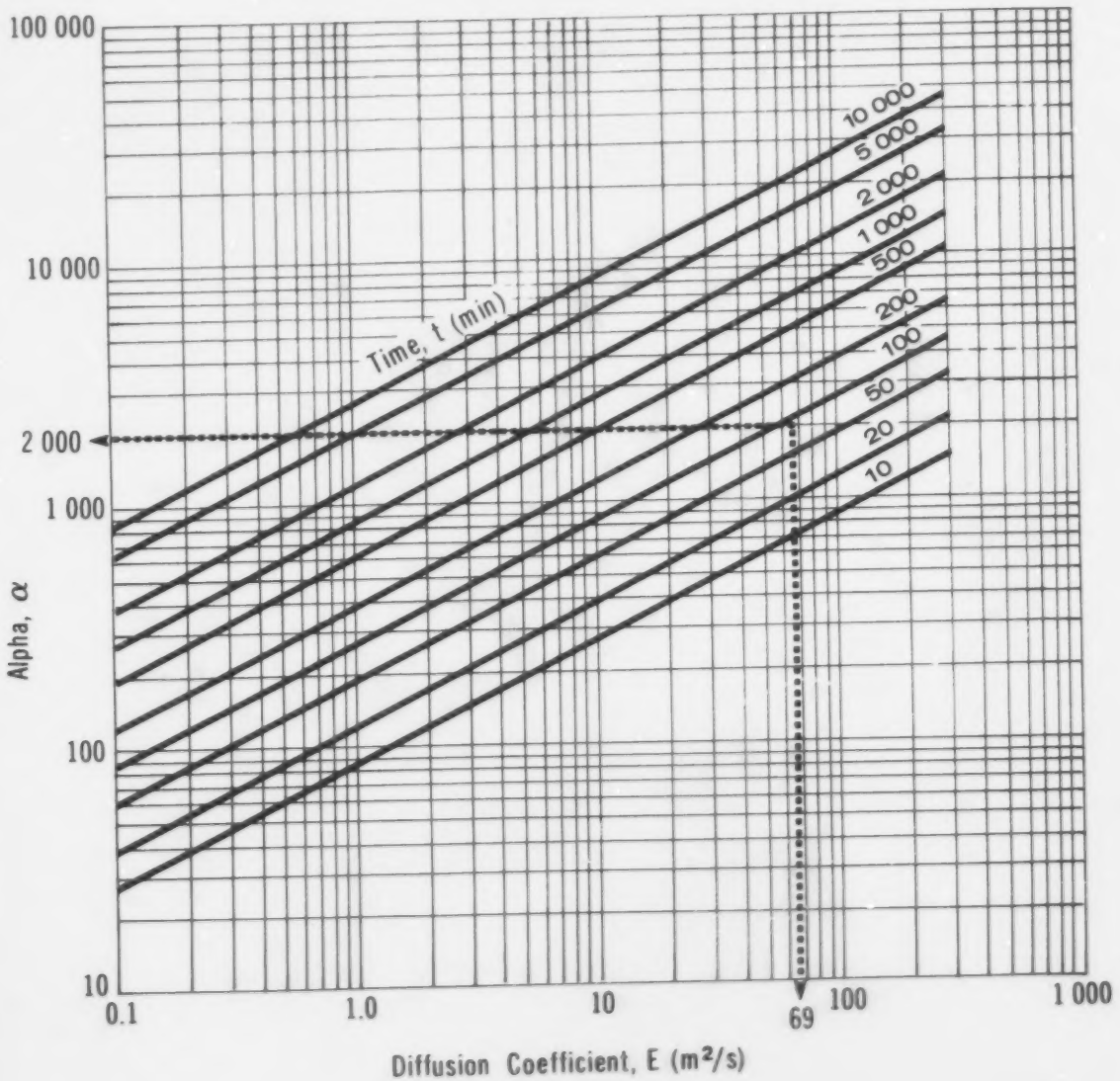


FIGURE 26

NITRIC ACID

ALPHA vs DELTA

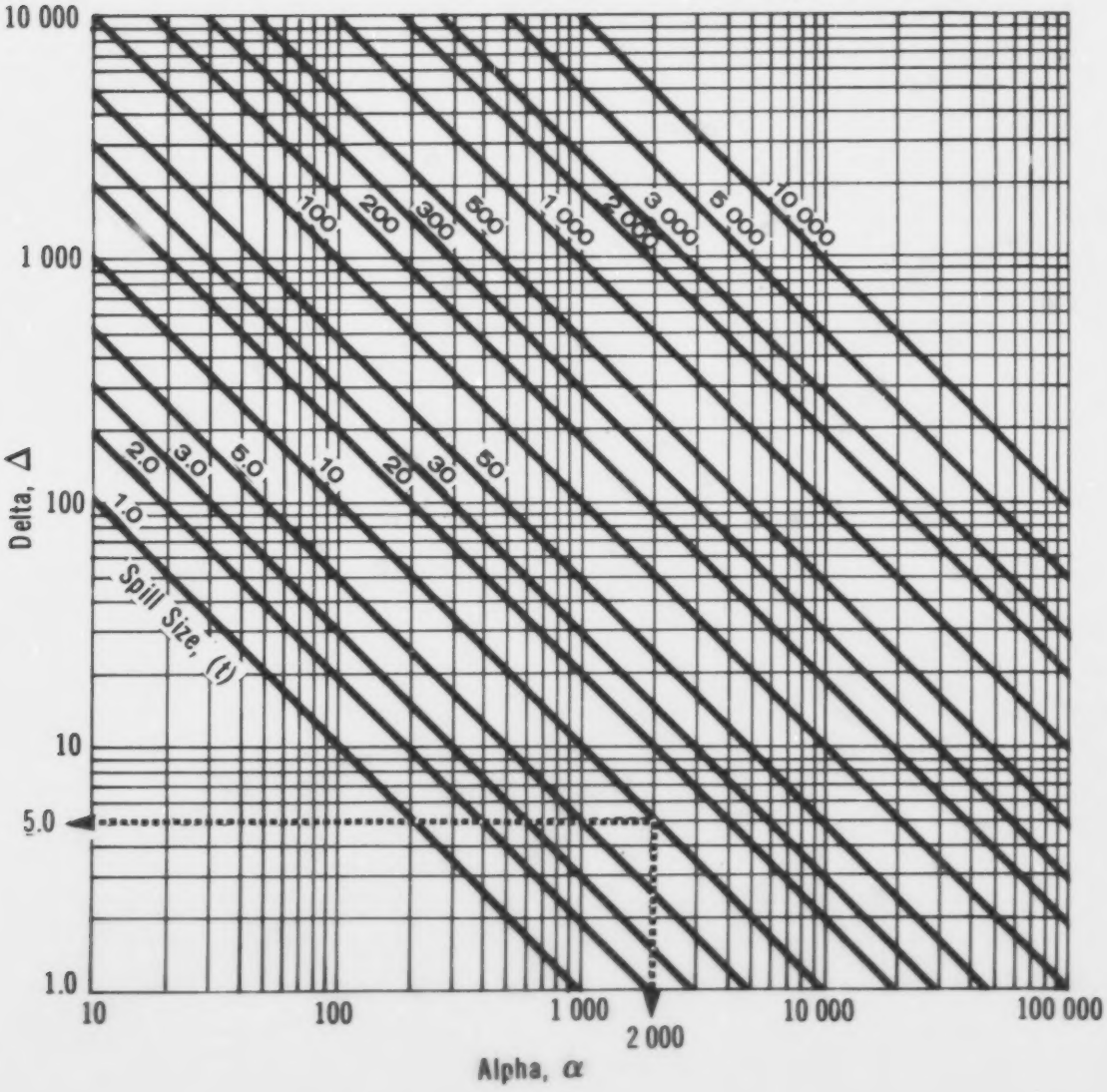


FIGURE 27

NITRIC ACID

MAXIMUM CONCENTRATION vs DELTA

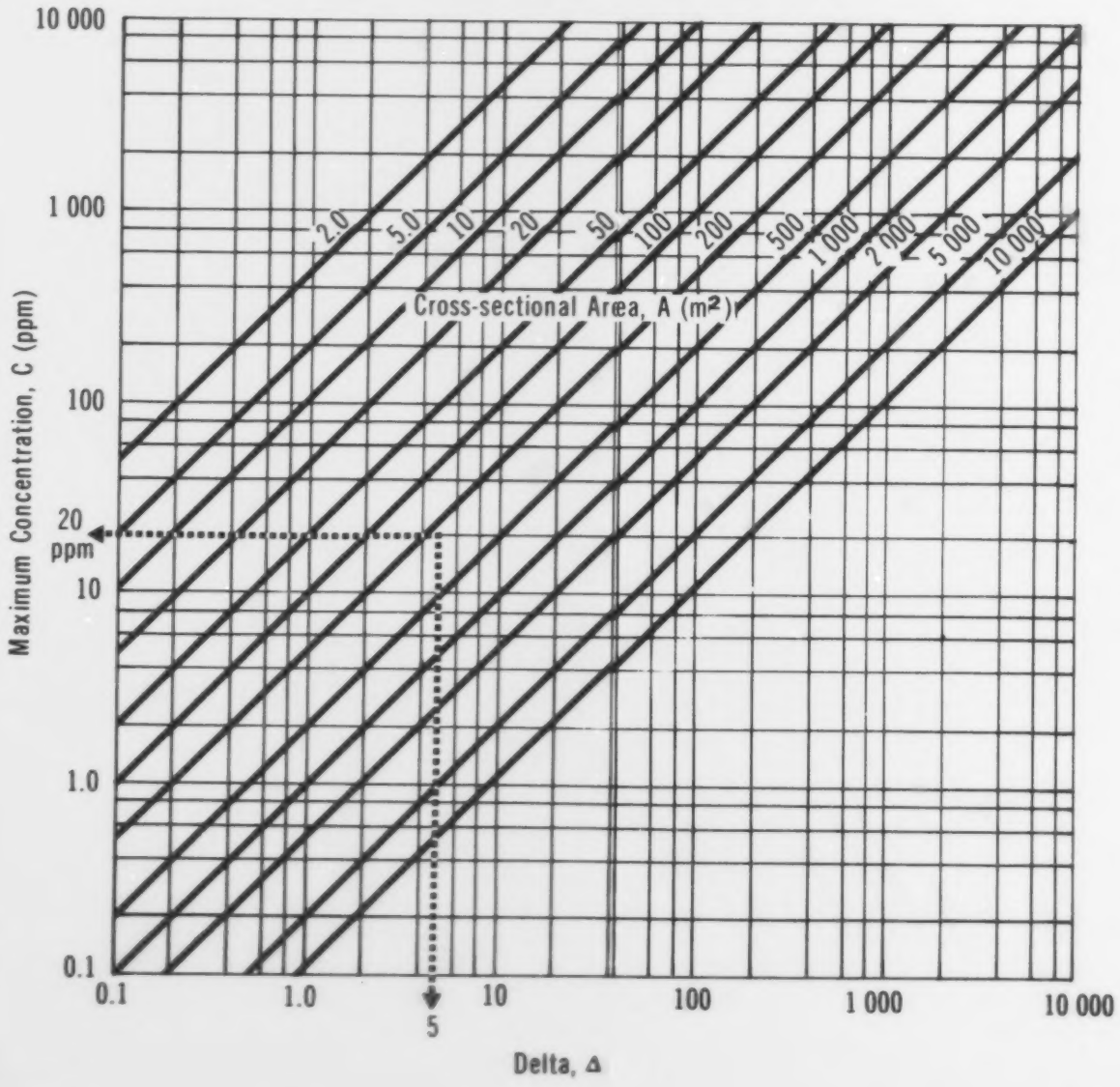


FIGURE 28

NITRIC ACID

VOLUME vs RADIUS

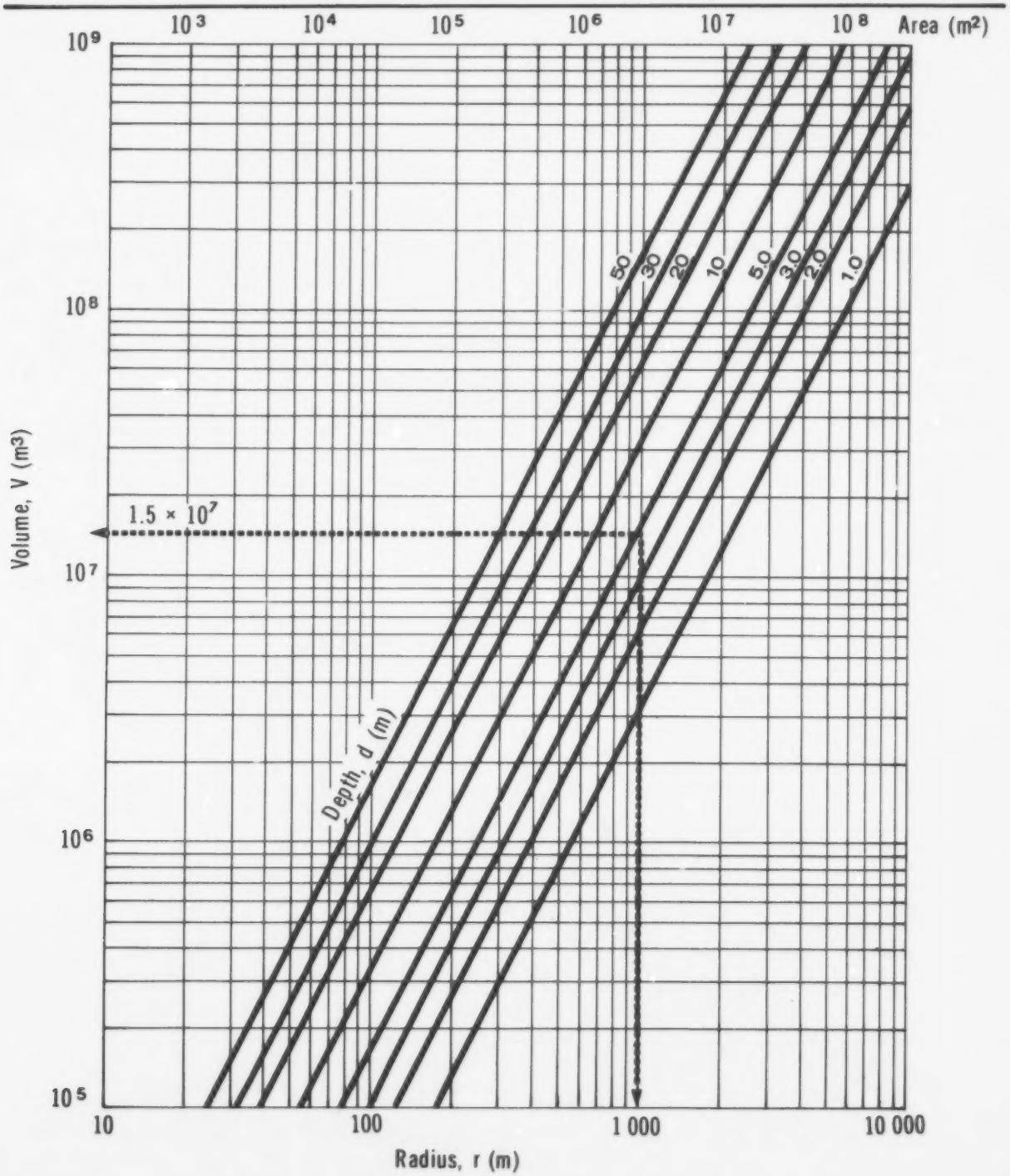
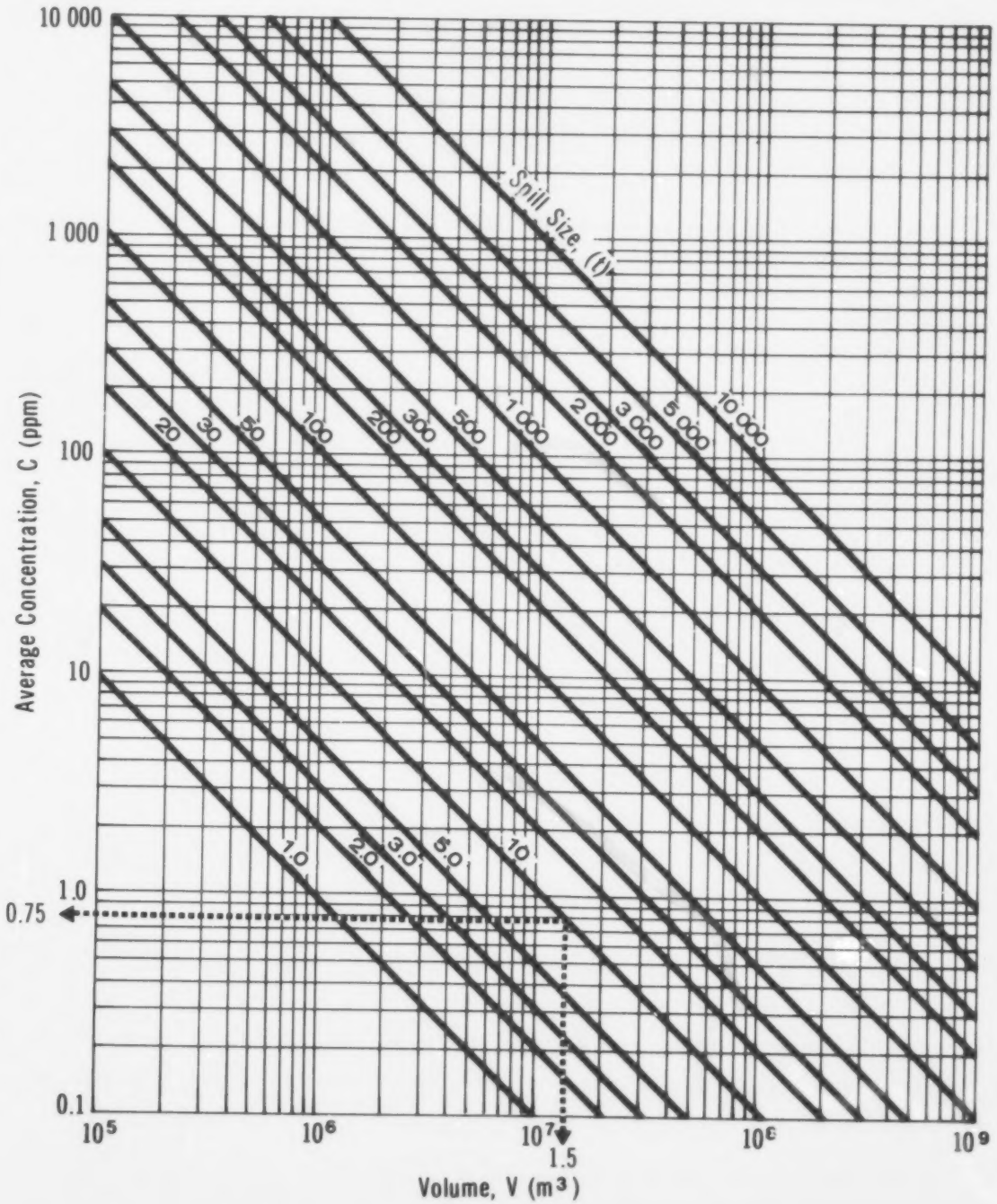


FIGURE 29

NITRIC ACID

AVERAGE CONCENTRATION vs VOLUME



depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- mass = 20 tonnes of 50 percent nitric acid solution, containing the equivalent of 10 tonnes of nitric acid

Step 2: Calculate time to reach the point of interest

- Use Figure 22
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 23
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 24
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 25
- With E = 69 m^2/s and t = 83 min, (α) = 2000

Step 6: Calculate delta (Δ)

- Use Figure 26
- With alpha (α) = 2000 and spill mass = 10 tonnes, delta (Δ) = 5

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 27
- With Δ = 5 and A = 250 m^2, C = 20 ppm

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 20 tonne spill of 50 percent nitric acid solution has occurred in a lake. The point of interest is located

on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 10 tonnes (equivalent weight of nitric acid)

Step 2: Determine the volume of water available for dilution

- Use Figure 28
- With r = 1000 m, d = 5 m, the volume (V) is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 29
- With V = 1.5×10^7 m^3 and spill mass = 10 tonnes, the average concentration is 0.75 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of nitric acid onto soil and its transport downward through the soil are presented here.

Nitric acid is shipped in various grades ranging from 52 to 98 percent by weight. It mixes with water and, when spilled onto soil, infiltrates readily. Precipitation falling at the time of the spill or water used to flush the site will dilute the infiltrating acid. If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled nitric acid will run off or remain ponded.

For this work, the soils have been assumed to be at field capacity (the maximum amount of water the soil will hold after the excess is drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport through the soil, nitric acid will dissolve some of the soil material, in particular the carbonate-based materials. The acid will be neutralized to some degree, with adsorption of the proton also occurring on clay materials. However,

significant amounts of acid are expected to remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors.

Upon reaching the groundwater table, the acid will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and dispersion serving to reduce the acid concentration. This is shown schematically in Figure 30.

5.5.2 Equations Describing Nitric Acid Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Nitric Acid in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa·s)

g = acceleration due to gravity = 9.81 m/s^2

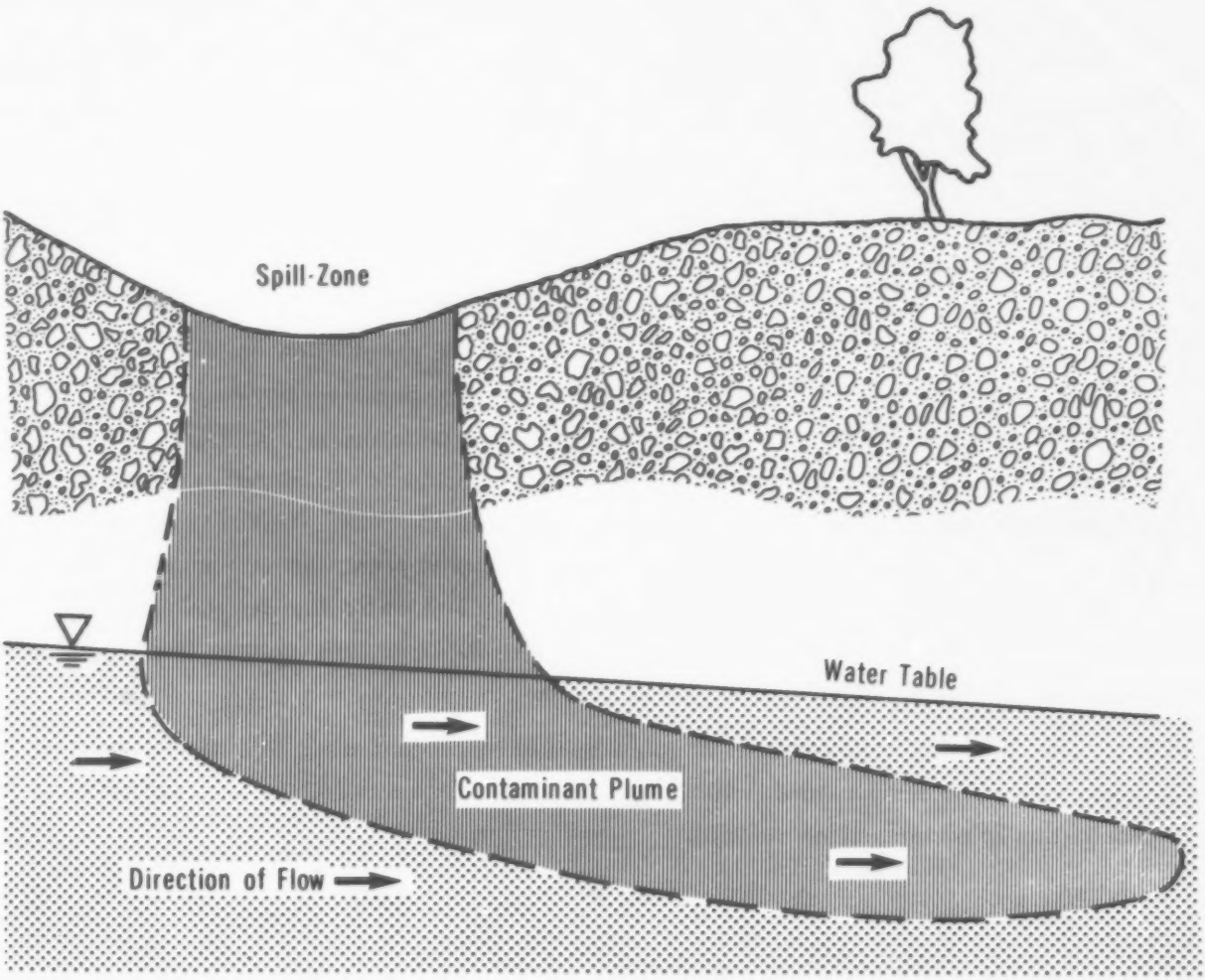
The fluids involved are 60 percent and 10 percent by weight nitric acid, and water. The water calculations represent the extreme as nitric acid is diluted. The appropriate properties of nitric acid are given in the chart below.

	Nitric Acid			
	60 percent by Wt.		10 percent by Wt.	Water
Property	20°C	4°C	20°C	20°C
Mass density (ρ), kg/m^3	1374	1400	1061	998
Absolute viscosity (μ), Pa·s	2.4×10^{-3}	3.2×10^{-3}	1.23×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.56 \times 10^7)k$	$(0.43 \times 10^7)k$	$(0.84 \times 10^7)k$	(0.98×10^7)

FIGURE 30

NITRIC ACID

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of nitric acid into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 31. The nomograms are presented as Figures 32, 33 and 34. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p. It is a limiting condition as nitric acid becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of 60 percent nitric acid has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 24 minutes after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 24 min

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.1 m at t_p = 24 min
- Groundwater table has not been reached in this time

FIGURE 31

NITRIC ACID

FLOWCHART FOR NOMOGRAM USE

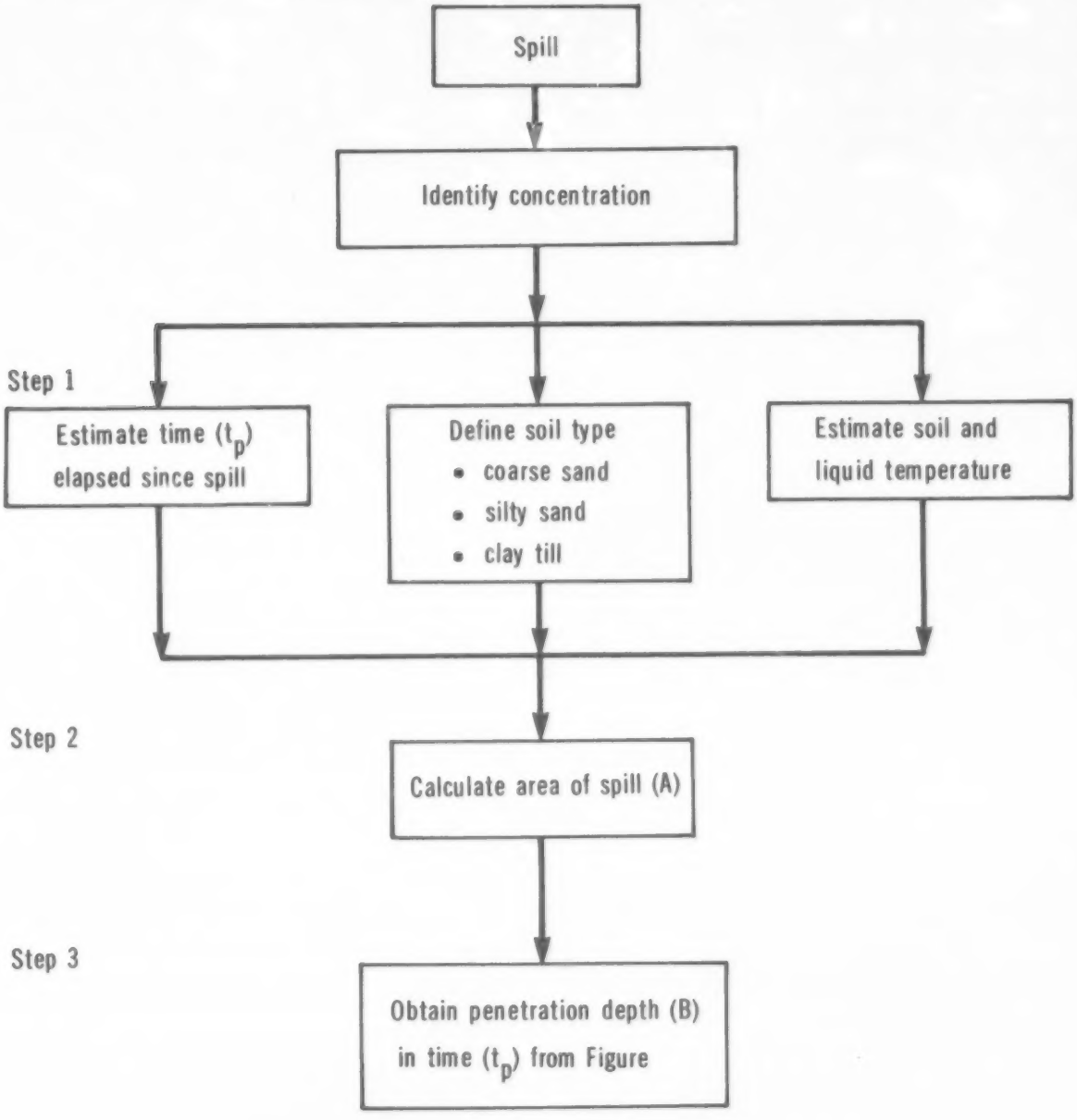


FIGURE 32

NITRIC ACID

PENETRATION IN COARSE SAND

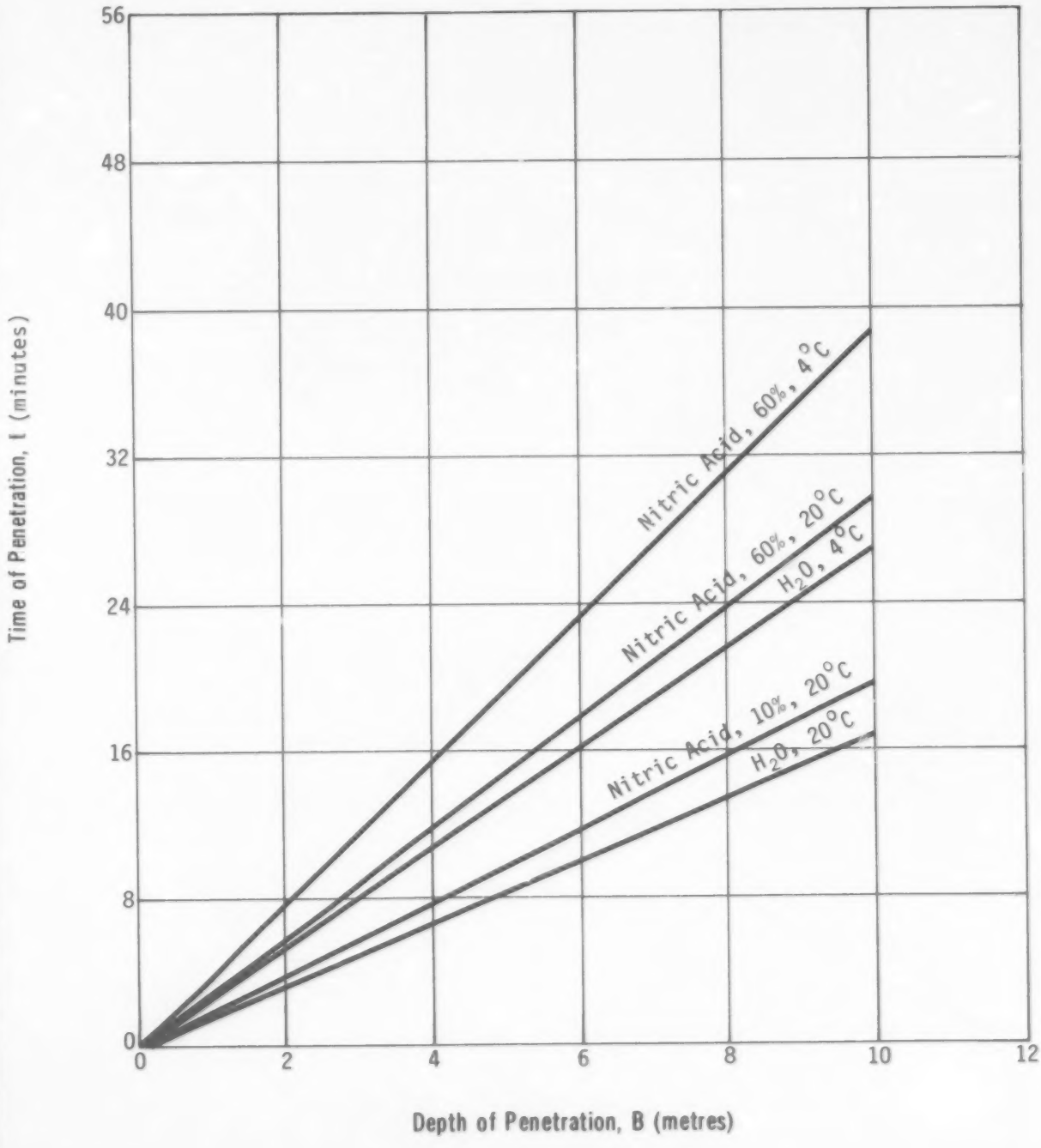


FIGURE 33

NITRIC ACID

PENETRATION IN SILTY SAND

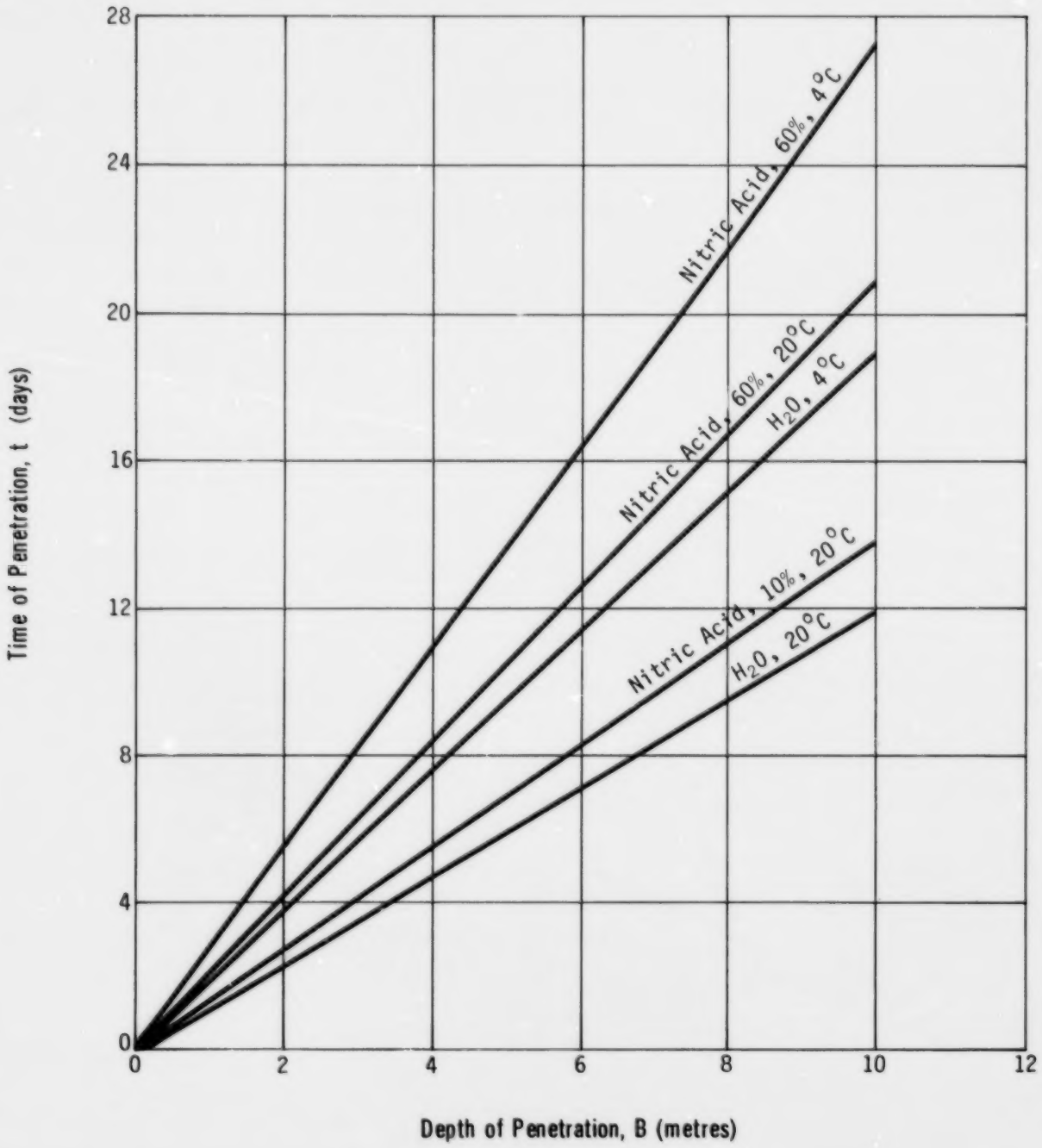
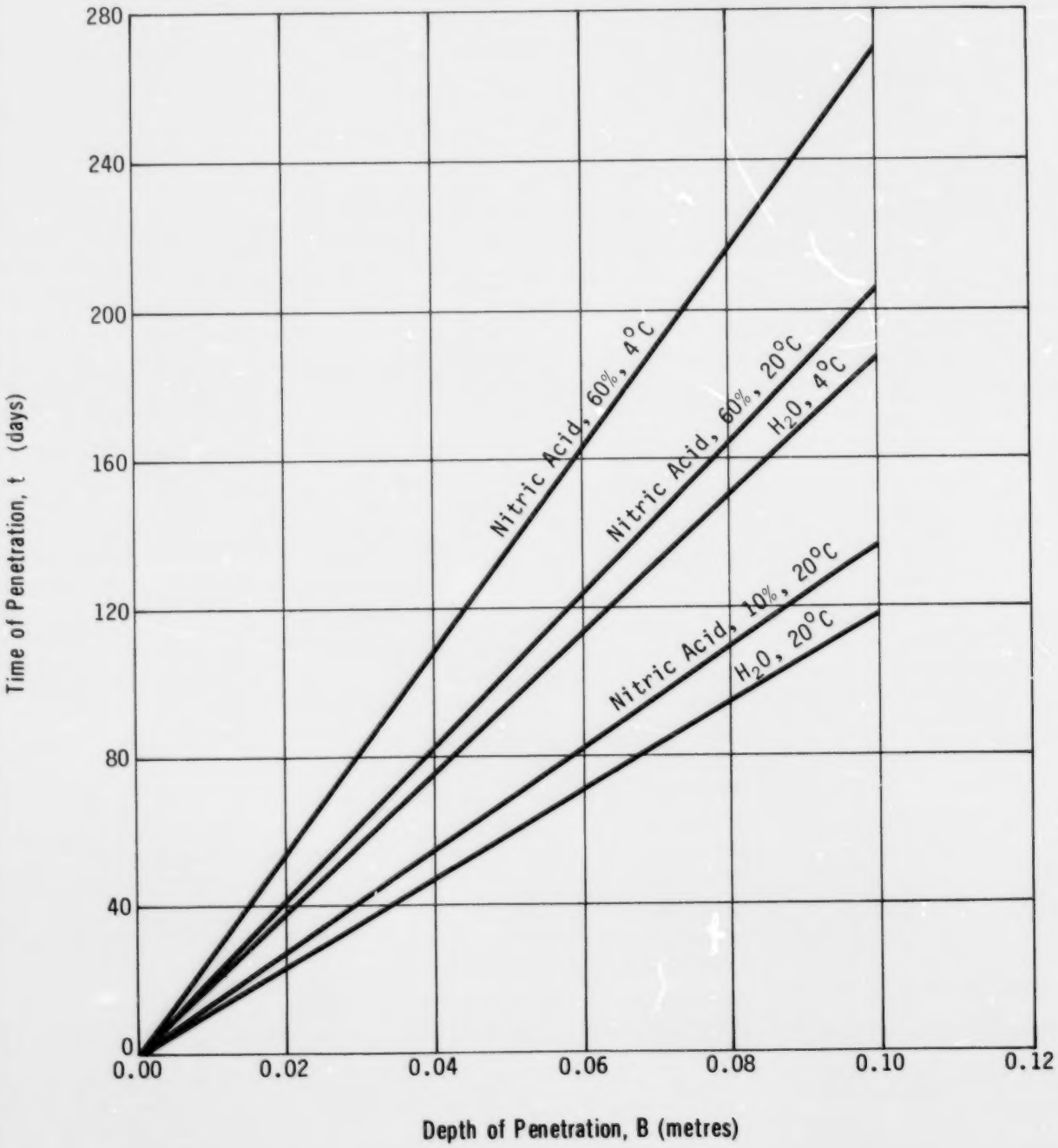


FIGURE 34

NITRIC ACID

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Nitric acid is not specifically regulated in Canada; however, 10 mg/L nitrate as nitrogen and a pH minimum of 6.5 have been recommended federally and in Ontario (Guidelines/Canadian/Waters 1978; Water Management Goals 1978). A maximum nitrate/nitrogen level of 10 ppm is also recommended in the United States (Drinking Water Standards 1973).

6.1.2 Air. The Ontario environmental limit (half-hour point of impingement) for nitric acid is 100 $\mu g/m^3$ of air (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Nitric acid has been assigned a TL_m96 of 10 to 100 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
750	0.50 to 0.84	Goldfish	lethal	pH 3, hard	Ellis 1937. IN OHM-TADS 1981
pH 4.4	7	Minnows *(Phoxinus phoxinus)*	survival time	-	Jones 1969
pH 4.6	7-7.5	Minnows *(Phoxinus phoxinus)*	survival time	-	Jones 1969
pH 4.8	7.5	Minnows *(Phoxinus phoxinus)*	survival time	-	Jones 1969
pH 5.0	27.5-21	Minnows *(Phoxinus phoxinus)*	survival time	-	Jones 1969
pH 5.2-5.8	>30 d	Minnows *(Phoxinus phoxinus)*	no effect	-	Jones 1969

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests (Freshwater)					
1.6	not stated	Trout	toxic		WQC 1963
15.6	24	Trout	toxic		WQC 1963
72	96	Mosquito fish	TL_m	pH 6.2, turbid	WQC 1963
1000	0.5	Trout	toxic	tap	WQC 1963
20		Carp, goldfish	not harmful		WQC 1963
200	> 96	Goldfish	not harmful	pH 4.9	WQC 1963
Microorganisms					
107	not specified	Daphnia	threshold for immobilization	-	WQC 1963
Invertebrates (saltwater)					
180	48	Shore crab	LC_{50}	static, aerated	WQCDB-5 1973
330 to 1000	48	Cockle	LC_{50}	aerated	Portman 1970
100 to 330	48	Starfish	LC_{50}	aerated	Portman 1970
100 to 330	48	Armed bullhead	LC_{50}	static, aerated	OHM-TADS 1981
100 to 330	48	Pugge	LC_{50}	aerated	OHM-TADS 1981

6.3 Other Land and Air Toxicity

Nitric acid is toxic to all species; nitrate can be toxic to animal life even after neutralization (OHM-TADS 1981).

6.4 Effect Studies

6.4.1 pH Effects. The effect of pH on the aqueous environment is generally well known due to studies associated with acid deposition. It is generally known that a fish kill

results when the pH of a water body is lowered rapidly, such as would be the case after a spill of nitric acid. The effect of a gradual pH decrease is also well documented, namely declining fish populations and lower productivity of phytoplankton communities. In water bodies with poor buffering qualities, community changes further reduce the availability of nutrients because of decreased remineralization of detritus. As would be expected, the extent of the overall damage would be influenced by the amount of acid introduced into the water body, the buffering ability of the body, the rate of dilution due to water flow, and the time required for man-initiated neutralization and general cleanup.

Generally, a pH lower than 5 is lethal to most fish, the effects differing according to the species and to the stages of life history in a given species. In Norway, for example, a study of lakes with varying pH levels showed a very rapid increase in the percentage of lakes at the 5.0-5.5 pH range which contained no fish . The mechanisms of pH effects on fish are not completely understood; however, interference with the metabolism of calcium, sodium and other elements has been strongly implicated. Invertebrates are also threatened at pHs lower than 5.0; because these organisms are an important component of aquatic food webs, pH levels at or below 5.0 for an extended period in a water body could pose a very serious threat to aquatic ecosystems. Limited data are available on the effects of pH on algae, but evidence does indicate that a lower pH would favour species normally excluded by lack of free carbon dioxide. At pH levels below 4.5, growth of most species would be reduced and the result would be erratic blooms by the few tolerant species remaining. The reader is advised to also review Section 6 of the Sulphuric Acid and Oleum, Hydrogen Chloride, and Hydrochloric Acid manuals for additional comments on and data regarding pH effects. pH effects on fish are summarized below:

pH	Effects
5.0 - 6.0	Not harmful unless >20 ppm CO_2 or high concentrations of iron hydroxides are present.
5.5 - 6.0	Eastern brook trout survive; rainbow trout do not occur; growth rate of carp is reduced; spawning is reduced; molluscs are rare.
5.0 - 5.5	Smaller populations of fish, but not lethal; may be lethal to eggs or larvae and some invertebrates; algae and higher plants will grow.
4.5 - 5.0	Harmful to salmonid eggs and fry; harmful to common carp; tolerable lower limit for most fish; lethal to some invertebrates.

pH	Effects
4.0 - 4.5	Harmful to salmonids, tench, bream, roach, goldfish, common carp; resistance increases with age. Pike can breed, but perch, bream and roach cannot.
3.5 - 4.0	Lethal to salmonids. Roach, tench, perch, pike survive; all flora and fauna severely restricted.
3.0 - 3.5	Toxic to most fish; some plants and invertebrates survive.

(WQC 1972; Beamish 1976; Grahn 1974; Gorham 1963; NRC 1978; Likens 1976; Hendry 1976; Giddings 1976; Moss 1973a, b; EIFAC 1969)

6.4.2 Nitrate (NO_3^-) Effects. The ecological effects of nitrate can be beneficial or detrimental. Nitrogen is an essential nutrient for biotic activity; however, in some natural ecosystems such as lakes and estuaries, the addition of nitrogen can contribute to eutrophic conditions that are considered undesirable. The introduction of nitrate as nitric acid will not only increase the nitrate concentration, but also increase the acidity of the water body. Eutrophication of surface waters results in quality changes such as algal blooms, the depletion of dissolved oxygen in bottom water, a decrease in water clarity, the loss of cold water fisheries, shortened food chains, and takeover by rough fish. Nitrogen appears to be a limiting nutrient in some marine coastal waters; additions of nitrate to such systems will stimulate primary production and can produce changes in the dominant species of plants, leading to cultural eutrophication and ultimately to deterioration of water quality. In general though, the specific contribution of nitrate to eutrophication is uncertain because of a relative lack of data on nitrate inputs *per se* and because of the ease of interconversion of nitrogen forms. It is safe to say that the relative effect of nitrate in water or on land as the result of a spill would be far outweighed by the effect of the acidic properties of the chemical (NRC 1978; Brezonick 1969).

The nitrate ion is known to be toxic to animals. The chronic animal toxicity limit is 200 ppm (NO_3^- threshold); the concentration found toxic to livestock is 400 ppm (NO_3^- limiting) (OHM-TADS 1981).

6.5 Degradation

Nitric acid may be slowly neutralized by hardness minerals (Ca and Mg) in some waters. The nitrate ion, however, may persist longer but will ultimately be

consumed as a plant nutrient. Low pH may interfere with coagulation in water treatment processes (OHM-TADS 1981).

6.6 Long-term Fate and Effects

High nitrate levels will stimulate plankton and aquatic weed growth and thus may foster fish production (WQC 1963). If sufficient algal bloom occurs, eutrophication may result (OHM-TADS 1981).

7 HUMAN HEALTH

Nitric acid is highly irritating to eyes, skin and mucous membranes, and can cause severe burns and tissue corrosion on contact. It is also highly corrosive to the teeth. It is reported as being one of the more hazardous of the mineral acids, partly because it does not set up a violent respiratory reflex which serves as a warning of danger (TDB (on-line) 1981).

The toxicity of the compound has recently been reviewed in a NIOSH Criteria Document (NIOSH 1976). No data were found in the literature concerning nitric acid's potential as a teratogen, mutagen or carcinogen. The compound is included in the EPA TSCA Inventory.

The toxicological data summarized here has been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for nitric acid are based upon its potential as a skin, nasal, lung and eye irritant and upon its corrosive effect on teeth. It is possible that these exposure standards may not prevent the potentiation of nitrogen dioxide effects (Doc. TLV 1981). Canadian provincial guidelines are generally similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighed Averages (TWA)			
TLV® (8 h)	USA-ACGIH	2 ppm (5 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	2 ppm	NIOSH/OSHA 1981
TWA (10 h)	USA-NIOSH	2 ppm (5 mg/m^3)	NIOSH 1976
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	4 ppm (10 mg/m^3)	TLV 1983

Guideline (Time)	Origin	Recommended Level	Reference
Other Human Toxicities			
IDLH	USA-NIOSH/OSHA	100 ppm	NIOSH Guide 1978
LD_{LO} (oral)	-	430 mg/kg	RTECS 1979
Fatal	-	1 teaspoonful to 1/2 ounce of concentrated chemical, but even a few drops may be lethal if they gain entry into the trachea.	TDB (on-line) 1981

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows, using figures for 100 percent nitric acid:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV•, in ppm)

At 20°C, ITI = 1315.12 (48 mm Hg/2 ppm)

At 20°C, ITI = 3.15×10^4

7.2 Irritation Data

7.2.1 Skin Effects.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Concentrated	Destroys tissue because of its corrosive chemical properties. Skin contact produces burns; a change in skin colour will occur from contact with the acid at lower concentrations.	McAdams and Krop 1955; Fairhall 1957. IN NIOSH 1976
"Dilute solution"	Produces a mild irritation of the skin and tends to harden the epithelium without destroying it.	Fairhall 1957. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
Unspecified	Burns	Rambousek 1913. IN NIOSH 1976
Unspecified	Ulcers	NIOSH/OSHA 1981
Unspecified	Local irritation, yellow discolouration of the skin, severe burns, and necrosis.	ITII 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	In contact with the eye, concentrated nitric acid causes immediate opacification of the corneal and conjunctival epithelium.	Grant 1962. IN NIOSH 1976
Unspecified	In severe cases, may result in permanent corneal opacification with attendant blindness, fusion of the eyelids, and shrinkage of the eyeball.	Ask 1925. IN NIOSH 1976
Unspecified	Conjunctivitis, corneal ulcers, burns and necrosis of tissue of the eye.	ITII 1981

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Acrid (DuPont 1980). Acrid, choking, suffocating (CCD 1977).

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Taste Detection Threshold	in water	1×10^{-3} Normality	ASTM 1980

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
2 to 25 ppm (8 h)	Pulmonary irritation and symptoms of lung damage.	GE 1980
Unspecified	Variable degree of upper respiratory irritation, which may or may not be manifested immediately. Signs exhibited immediately following exposure included dryness of the throat and nose, cough, chest pain, and dyspnea. A latent period of up to 24 hours has been reported.	Hall and Cooper 1905; Zadek 1916; Schussler 1935. IN NIOSH 1976
Unspecified	Pulmonary edema.	Schussler 1935. IN NIOSH 1976
Unspecified	Two cases. Only minor respiratory symptoms during and after exposure followed by severe cyanosis, dyspnea, chest pain and cough. Death occurred in one case after a delay of a week or more.	Ask 1925. IN NIOSH 1976
SPECIES: Rat		
244 ppm (as NO_2) (30 min)	LC_{50}. Exposed to white fuming nitric acid (0.1 to 0.4 percent NO_2).	RTECS 1979
138 ppm (as NO_2) (30 min)	LC_{50}. Exposed to red fuming nitric acid (8 to 17 percent NO_2).	NIOSH 1976
65 ppm (as NO_2) (4 h)	LC_{50}. Exposed to red fuming nitric acid.	RTECS 1979
25 ppm (HNO_3 vapour) (no time, single exposure)	No apparent effect.	NIOSH 1976
SPECIES: Mouse		
244 ppm (30 min)	LC_{50}. Exposed to white fuming nitric acid.	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
67 ppm (4 h)	LC_{50}. Exposed to red fuming nitric acid.	RTECS 1979
Chronic Exposures		
SPECIES: Human		
Unspecified	Continued exposure may cause a chronic bronchitis; more severe exposure may cause a chemical pneumonitis. These effects are not well established because reports of exposures to nitric acid vapour per se as opposed to vapour and gases generated by the decomposition of nitric acid have not been found in the literature.	Fairhall 1957. IN NIOSH 1976
SPECIES: Rat, Mouse, Guinea Pig		
17 000 and 26 000 $\mu g/m^3$ (9 and 14 ppm, 4 h/d, 5 d/wk, 6 wk)	Increased lung pathology.	Gray 1952. IN USEPA 1978

7.4.2 Ingestion. The ingestion of nitric acid results in immediate tissue destruction accompanied by side effects that may lead to death within a relatively short period of time. The ingestion of large amounts of aqueous nitrate ion (NO_3^-) causes methemoglobinemia (excessive production of abnormal hemoglobin), characterized by cyanosis and anoxia due to the defective transport of oxygen by high levels of circulating methemoglobin. Methemoglobin is a product of hemoglobin in which the ferrous iron is oxidized to the ferric form and thus no longer allows oxygen to reversibly bind to red blood cells. Since nitrate ion remains after neutralization of nitric acid, it is considered appropriate to include data concerning this species in this manual. Nitrate ion is converted to nitrite ion (NO_2^-) by bacteria present in human saliva. Ruminants are much more susceptible to the toxic effects of nitrate than are nonruminants. This probably results from the longer retention time and greater opportunity for reduction in the rumen.

The role of excess nitrate in the nitrogen cycle is well known and not the subject of this manual (NRC 1981).

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
"1/2 cup"	Case of attempted suicidal ingestion, in which patient survived. After a period of years, the patient developed classical pernicious anemia, presumably due to the destruction of the gastric mucosa with its vital intrinsic factor secreting function.	Alsted 1937. IN NIOSH 1976
<30 mL	Victim died 2 weeks after gargling with nitric acid and swallowing a small amount. Gastric hemorrhage, destruction of inner lining of oesophagus.	Holinger et al. 1953. IN NIOSH 1976
1 teaspoonful to 1/2 ounce	The amount of concentrated acid fatal to adults, although even a few drops may be lethal if the acid gains access to the trachea.	TDB (on-line) 1981
4 to 50 g/60 kg as NO_3^-	Lethal level.	NRC 1981
2 to 4 g as NO_3^-	Toxic dose (toxic dose is a single dose that will induce methemoglobinemia).	NRC 1981
SPECIES: Rat		
1 percent HNO_3 solution (0.15 mL) (intratracheal injection)	24 h post injection, increased inflammation of bronchioles; epithelium lost normal scalloped appearance. Increased cytoplasm in epithelium. Inflammed alveolar septae. No difference in lung wet and dry weights. HNO_3 enhanced pulmonary absorption rates of p-aminohippuric acid, procaineamide ethobromide, procaineamide and mannitol.	Gardiner 1976. IN USEPA 1978

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Mouse		
12 300 mg/L as $NaNO_3$ in distilled water (25 wk)	Lung tumours were similar in the experimental and control mice ($NaNO_3$ solution was substituted for drinking water). Mice were killed 13 weeks after experiment was concluded.	NRC 1981
25 000 and 50 000 mg $NaNO_3$/kg of diet for lifetime	No significant difference in tumours from those of control animals.	NRC 1981
40 mg ($NaNO_3$) daily in drinking water (84 wk) (15 male, 15 female)	Increase in pituitary adenomas in treated females (not statistically significant). Mice were killed 20 weeks after experiment was concluded.	NRC 1981
SPECIES: Rat		
10 000 mg $NaNO_3$/kg in diet (2 yr)	No effect level.	NRC 1981
50 000 mg $NaNO_3$/kg in diet (2 yr)	Mild retardation of growth.	NRC 1981
SPECIES: Dog		
20 000 mg $NaNO_3$/kg in diet for 105-125 d	No effect level.	NRC 1981

7.4.3 Dental Erosion.

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Human		
Unspecified	Study of 783 workers, only 32 of whom were exposed to nitric acid alone. Of these,	NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
	9 percent had active dental erosion compared to no active dental erosion in the control group of 293 unexposed workers.	
Unspecified	26 of 31 exposed workers showed traces of dental erosion. Four of the five with none had been employed for less than a year.	Dettling 1935. IN NIOSH 1976

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity. There are no hard data to indicate that nitrate (NO_3^-) is carcinogenic or directly mutagenic. There is strong evidence that nitrate is reduced to nitrite (NO_2^-) by bac eria present in human saliva. Nitrite, along with nitrosamines, appears to be more closely linked to carcinogenicity and mutagenicity (NRC 1981). No data were found with respect to teratogenicity.

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of mucous membranes and respiratory tract.
2. Dryness of throat and nose (NIOSH 1976).
3. Cough.
4. Chest pain.
5. General malaise (NIOSH 1976).
6. Dental erosion.
7. Dyspnea.
8. Cyanosis.
9. Pulmonary edema (NIOSH 1976).
10. Bronchopneumonia.
11. Pulmonary fibrosis.

12. Chemical pneumonitis (Doc. TLV 1981).
13. Coma (TDB (on-line) 1981).
14. Convulsion (TDB (on-line) 1981).
15. Death.

7.5.2 Ingestion.

1. Vomiting.
2. Colic.
3. Purgation (TDB (on-line) 1981).
4. Abdominal tenderness (TDB (on-line) 1981).
5. Tongue raw and swollen (TDB (on-line) 1981).
6. Impairment of the airway, making speech and swallowing extremely painful (TDB (on-line) 1981).
7. Severe damage to mouth, pharynx, oesophagus and stomach.
8. Prostration (TDB (on-line) 1981).
9. Acute shock.
10. Death.

7.5.3 Skin Exposure.

1. Irritation.
2. Hardening of the epithelium (NIOSH 1976).
3. Yellow discolouration.
4. Ulcers.
5. Burns.
6. Necrosis.

7.5.4 Eye Exposure.

1. Irritation.
2. Conjunctivitis.
3. Corneal opacity.
4. Conjunctival epithelium opacity (NIOSH 1976).
5. Burns.
6. Fusion of eyelids and shrinkage of eyeballs (NIOSH 1976).
7. Blindness.

7.6 Human Toxicity to Decay or Combustion Products

Solid nitric acid is stable. Liquid nitric acid will decompose to varying degrees at any temperature above its melting point. Gaseous nitric acid decomposes similarly. Aqueous nitric acid, although more stable than the pure liquid, will gradually turn yellow to brown, indicating the presence of nitrogen dioxide (NO_2). Some of the degradation of aqueous nitric acid can be attributed to photochemical decomposition. The fuming acids evolve nitrogen dioxide vapours (Kirk-Othmer 1981; Bailar 1973; CPIA 1970). Other references refer to "acid fumes" evolving from the reaction of nitric acid with various materials, e.g., metals (Ashland MSDS 1977; NIOSH 1976). The latter were not defined, but certainly can be described as oxides of nitrogen. It is felt the primary product of decomposition is nitrogen dioxide (NO_2), but varying amounts of nitric oxide (NO) and dinitrogen tetroxide (N_2O_4) may also be present.

7.6.1 Nitric Oxide, Nitrogen Dioxide and Dinitrogen Tetroxide. Nitric oxide is a colourless gas with a sharp, sweet odour. It combines with hemoglobin which is oxidized in the blood to methemoglobin, with resulting anoxia. Nitric oxide is only slightly irritating to the upper respiratory tract and eyes; dangerous amounts of fumes may therefore be inhaled before any discomfort is noticed (Sax 1968). In air, nitric oxide is oxidized to nitrogen dioxide which is four to five times as toxic as nitric oxide (Patty 1963). The TLV® for nitric oxide is 25 ppm (8 h - TWA) and 35 ppm (STEL) (TLV 1983).

At normal environmental temperatures, nitrogen dioxide and dinitrogen tetroxide are always found together (proportion of NO_2 to N_2O_4 at 37.5°C is 3:7) (Sax 1968). At higher temperatures, the proportion of NO_2 increases. Mixtures are often referred to as "nitrogen dioxide", which is red-brown with a pungent, acrid odour, while dinitrogen tetroxide is colourless. Nitrogen dioxide undergoes thermal decomposition to nitric oxide and oxygen beginning at 150°C and is complete at 600°C (Cotton 1972). Nitrogen dioxide is mildly irritating to the eyes, nose and upper respiratory mucosa; therefore, dangerous amounts of fumes may be inhaled before any discomfort is noticed. Nitrogen dioxide reacts with water to form nitric and nitrous acids; the latter decomposes to form nitric acid, nitric oxide and water, especially when warmed (Cotton 1972). These acids are formed deep in the respiratory system where they irritate the lungs, causing congestion of the throat and bronchi, and edema of the lungs. Symptoms of exposure include weakness, nausea, abdominal pain, cough, mucoid frothy sputum, accelerated heart action, severe cyanosis and convulsions. Excessive exposures will result in death from asphyxia. Immediate symptoms may clear up on breathing fresh air; however, the

symptoms previously described may ensue in 6 to 24 hours. In fatal cases, death occurs within 8 to 48 hours following exposure. The TLV• for NO_2 is 3 ppm (8 h - TWA), and 5 ppm (STEL) (TLV 1983). There is no TLV• for nitrogen tetroxide.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire					•	•							Noncombustible. Upon decomposition, highly toxic fumes of nitrogen oxides may be emitted.	SAX 1979
Heat					•	•							Noncombustible. When heated to decomposition, highly toxic fumes of nitrogen oxides may be emitted.	SAX 1979; NFPA 1978
Seawater (Fuming Acids)	•						•						Will produce large quantities of nitrogen oxides.	CPIA 1970
Water or Steam	•		•			•		•					Will produce toxic, corrosive and flammable vapours.	SAX 1979; Bretherick 1979
SPECIFIC CHEMICALS														
Acetic Acid		•											If warm.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Acetic Anhydride			•										Mixtures with 50 to 85 percent fuming nitric acid are detonable and are sensitive to shock; other mixtures are also dangerous, but less so.	Bretherick 1979
Acetone		•											On contact with fuming HNO_3, acetone ignited.	Bretherick 1979
Acetone and Acetic Acid			•										Mixture of three will explode under certain conditions.	Bretherick 1979
Acetone and Sulphuric Acid			•										Mixture of three will explode under certain conditions.	Bretherick 1979
Acetonitrile			•										Highly explosive.	NFPA 1978
Acetylene			•					•					Trinitromethane is produced.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES OF GREATER TOXICITY	PRESSURIZATION OF SUBSTANCES VESSELS	SOLUBILIZATION IN CLOSED	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Acrolein							•						NFPA 1978
Acrylonitrile			•				•		•				Bretherick 1979; NFPA 1978
2-Alkoxy-1,3-Dithio-2-Phospholane		•										Ignite on contact.	Bretherick 1979
Allyl Alcohol	•						•					With 70 percent nitric acid.	NFPA 1978
Allyl Chloride	•						•					With 70 percent nitric acid.	NFPA 1978
2-Aminoethanol	•						•						NFPA 1978
Ammonia		•										Ammonia will ignite in nitric acid vapours.	Bretherick 1979
Ammonium Hydroxide	•						•					With 70 percent acid and 28 percent ammonium hydroxide.	NFPA 1978
Aniline		•										Aniline ignites spontaneously in presence of red fuming nitric acid.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Anilinium Nitrate									•				Mixture may possess high explosive properties.	Bretherick 1979
Antimony										•			With finely powdered antimony.	NFPA 1978
Arsine		•											Reacts explosively.	NFPA 1978
Arsine-Boron-Tribromide										•			Violently oxidized by nitric acid.	Bretherick 1979
1,4-Bis(Methoxy methyl)-2,3,5,6-Tetramethyl Benzene		•					•							Bretherick 1979
Bismuth											•		The metal may become red hot.	NFPA 1978
Boron									•				Incandescence occurs.	NFPA 1978
Boron Decahydride		•												NFPA 1978
Boron Phosphide	•													NFPA 1978
Bromine Pentafluoride										•				NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Butanethiol											•		Ignites with 96 percent HNO_3.	Bretherick 1979
n-Butyraldehyde	•							•					With 70 percent nitric acid.	NFPA 1978
Calcium Hypophosphite		•											Ignites on contact.	NFPA 1978
Carbon										•			Pulverized carbon.	NFPA 1978
Cellulose		•											May be converted to highly flammable nitrate ester on contact with HNO_3 vapour.	Bretherick 1979
Cesium Carbide			•										Mixture will explode.	NFPA 1978
Chlorobenzene			•										At temperatures above 80°C.	Bretherick 1979
4-Chloro-2-Nitroaniline						•	•						At temperatures above 30°C, decomposition occurs with evolution	Bretherick 1979

8.1 **Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)**

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
													of nitrous fumes and production of a very shock-sensitive explosive solid.	
Chlorine Trifluoride										•			With potassium salts and other items present.	NFPA 1978
Chlorosulphonic Acid	•							•					With 70 percent nitric acid.	NFPA 1978
Copper (I) Nitride										•			With concentrated acid.	Bretherick 1979
Cresol	•							•					With 70 percent nitric acid.	NFPA 1978
Crotonaldehyde		•											Ignites.	Bretherick 1979
Cumene	•							•					With 70 percent nitric acid.	NFPA 1978
Cupric (II) Nitride			•							•			Violent explosion.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Cyclohexanol		•											Violently explosive material is produced.	NFPA 1978
Cyclohexanone										•				NFPA 1978
Cyclohexylamine											•			Bretherick 1979
Cyclopentadiene		•												Bretherick 1979
1,2-Diamino-ethane bis-Tri-methyl Gold		•												Bretherick 1979
Diborane	•												Self-ignitable.	NFPA 1978
2,6-Di-t-Butyl-phenol		•											Forms explosive compound.	NFPA 1978
1,2-Dichloro-ethane		•											Mixtures are easily detonable by heat, impact or friction.	Bretherick 1979
Dichloromethane		•											A detonable solution is produced.	Bretherick 1979
Diethyl Ether		•											With *o*-bromotoluene and water present or with sulphuric acid present.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
3,6-Dihydro-1,2,2H-Oxazine		•											Product from reaction is explosive.	Bretherick 1979
Diisopropyl Ether	•						•						With 70 percent acid.	NFPA 1978
Dimagnesium Silicide										•			On contact.	Bretherick 1979
Dimethylamino-Methyl Ferrocene										•			Almost explosive reaction.	Bretherick 1979
Dimethyl Ether		•											Explosive mixtures may be produced.	Bretherick 1979
1,1-Dimethyl-hydrazine		•	•										Ignites or explodes on contact.	Bretherick 1979
Dimethyl Sulphide and p-Dioxane		•											Mixture of three explodes.	Bretherick 1979
Diphenyldistibene		•	•										Ignited in air and oxidized explosively with HNO_3.	Bretherick 1979
Diphenylmercury										•			At most temperatures.	Bretherick 1979
Diphenyl Tin		•											On contact.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Disodium Phenyl-orthophosphate			•										May form explosive picric acid derivatives.	Bretherick 1979
Divinyl Ether		•											Ignites rapidly.	Bretherick 1979
Epichlorohydrin	•							•					With 70 percent acid.	NFPA 1978
Ethyl Alcohol			•						•				Violent reaction that may accelerate to an explosion.	NFPA 1978
m-Ethylaniline		•											Ignites spontaneously.	NFPA 1978
Ethylene Diamine	•							•					With 70 percent acid.	NFPA 1978
Ethyleneimine	•							•					With 70 percent acid.	NFPA 1978
5-Ethyl-2-Methyl Pyridine			•					•					Explosive compound produced.	NFPA 1978
5-Ethyl-2-Picoline										•			Formation of an explosive compound from the reaction.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Ethyl Phosphine			•										With bromine or chlorine present.	NFPA 1978
Fat and Sulphuric Acid			•										Animal fat and two acids caused explosion.	Bretherick 1979
Ferrous Oxide											•		Oxide becomes incandescent on warming with nitric acid.	NFPA 1978
Fluorine		•	•			•							Decomposes with flame and may explode.	NFPA 1978
2-Formamide-1-Phenyl-1,3-Propanediol			•										Mixture can be detonated.	Bretherick 1979
Furfurylide Ketones		•											Ignite on contact.	Bretherick 1979
Furfuryl Alcohol		•											Ignites immediately.	NFPA 1978
Germanium										•			With powdered germanium.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Glycerol and Hydrofluoric Acid								•					Mixture of three reacts.	Bretherick 1979
Glyoxal	•							•					With 70 percent acid.	NFPA 1978
Hexalithium Disilicide			•										On contact.	Bretherick 1979
2,2,4,4,6,6-Hexamethyltrithiane			•							•			Explosively violent.	Bretherick 1979
Hexenol			•										Explodes on heating.	Bretherick 1979
Hydrazine		•											Ignites spontaneously.	NFPA 1978; Bretherick 1979
Hydrazoic Acid										•			Energetic reaction.	NFPA 1978
Hydrogen Iodide		•											Red flame is produced on contact.	NFPA 1978; Bretherick 1979
Hydrogen Peroxide and Ketones			•										Mixtures of three explode.	Bretherick 1979
Hydrogen Selenide		•											Incandescence occurs during ignition.	NFPA 1978; Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Hydrogen Sulphide		•											Incandescence.	NFPA 1978; Bretherick 1979
Hydrogen Telluride		•	•										Ignites, sometimes explosively.	NFPA 1978
Iron (II) Oxide		•											Incandescence.	Bretherick 1979
Indane and Sulphuric Acid			•										Mixture of three may explode.	NFPA 1978
Isoprene	•							•					With 70 percent acid.	NFPA 1978
Lactic Acid and Hydrofluoric Acid			•										Mixtures of the three are unstable.	Bretherick
Lead-containing Rubber		•											Ignition may occur.	Bretherick 1979
Lithium		•	•							•			Burns. May react vigorously to explosively.	NFPA 1978
Lithium Silicide			•			•							Nitrogen dioxide and silica are produced.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Magnesium			•										With finely divided magnesium.	NFPA 1978
Magnesium Phosphide											•		Oxidation occurs with incandescence.	NFPA 1978
Manganese		•	•										With powdered manganese, may accelerate to weak explosion.	NFPA 1978
Mesitylene	•		•										Forms an explosive compound.	NFPA 1978
Mesityl Oxide	•							•						NFPA 1978
4-Methylcyclohexanone			•							•				NFPA 1978; Bretherick 1979
Methylthiophene		•	•											Bretherick 1979
Neodymium Phosphide										•				NFPA 1978
Nitrobenzene			•										Very explosive.	NFPA 1978; Bretherick 1979
Nitromethane			•										Extremely explosive.	Bretherick 1979

8.1 **Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)**

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Oleum	•						•						With 70 percent nitric acid.	NFPA 1978
Organic Matter		•	•										Ignites spontaneously.	NFPA 1978; Bretherick 1979
Phosphine		•	•							•			Phosphine is violently decomposed. Explosion may occur.	NFPA 1978; Bretherick 1979
Phosphonium Iodide		•											Ignites spontaneously.	NFPA 1978
Phosphorus		•											Ignites.	NFPA 1978
Phosphorus Trichloride			•										On contact.	NFPA 1978
Phthalic Acid	•												With a fuming acid and sulphuric acid, reacts exothermically and may produce explosive compound.	NFPA 1978
Phthalic Anhydride	•												With a fuming acid and sulphuric acid, re-	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
													acts exothermically and may produce explosive compound.	
Polydibromosilane			•											Bretherick 1979
Polysilylene		•												Bretherick 1979
Potassium Hypophosphite			•										Explodes when evaporated with nitric acid.	NFPA 1978
Propiolactone (Beta)	•							•					With 70 percent acid.	NFPA 1978
Propylene Oxide	•							•					With 70 percent acid.	NFPA 1978
Pyrocatechol		•											Ignites on contact.	Bretherick 1979
Pyridine	•							•					With 70 percent acid.	NFPA 1978
Rubidium Carbide			•										Potential explosion.	NFPA 1978
Selenium									•				If organic matter present.	NFPA 1978
Selenium Iodophosphide			•											NFPA 1978

8.1 **Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)**

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Silver and Ethyl Alcohol			•										Presence of all three may produce detonable compound.	NFPA 1978
Silver Buten-3-ynide			•											Bretherick 1979
Sodium		•											Spontaneously with concentrated acid.	NFPA 1978
Sodium Azide										•			Energetic reaction.	NFPA 1978
Sodium Hydroxide	•						•						With 70 percent acid.	NFPA 1978
Stibine			•							•			Explodes with concentrated acid.	NFPA 1978
Sulphamic Acid										•			Release of nitrous oxide.	NFPA 1978
Sulphur Dioxide			•										Under certain conditions.	Bretherick 1979
Sulphuric Acid and Organic Materials										•			Possible explosion.	Bretherick 1979
Sulphuric Acid and Glycerides										•			Mixture of three may explode.	NFPA 1978

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Tetraboron Decahydride			•											NFPA 1978
Tetraphosphorus Triiodide		•								•			Burns and reacts vigorously.	NFPA 1978
Thiophene										•			Extensive oxidation occurs.	Bretherick 1979
Titanium			•										Residue from reaction with RFNA may explode.	NFPA 1978
Toluene			•							•			Explodes especially if sulphuric acid present.	NFPA 1978
Toluidine		•											Ignited by RFNA.	NFPA 1978
Triazine			•										Violent explosion with 99 percent acid at 36°C.	NFPA 1978
Tricadmium Diphosphide			•										On contact.	Bretherick 1979
Triethylgallium Monoetherate		•											Ignites spontaneously.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Trimagnesium Diphosphide											•		Oxidation occurs with incandescence.	Bretherick 1979
2,4,6-Trimethyl-trioxane										•			If mixing occurs rapidly.	Bretherick 1979
Turpentine		•											Ignites if catalyst is added.	Bretherick 1979
Unsymmetrical-Dimethylhydrazine			•										Ignites spontaneously.	NFPA 1978
Uranium			•							•				NFPA 1978
Uranium-Neodymium Alloy			•							•				NFPA 1978
Uranium-Neodymium-Zirconium Alloy			•							•				NFPA 1978
Uranium Disulphide										•				Bretherick 1979
Vinyl Acetate	•						•						With 36 percent acid.	NFPA 1978
Vinylidene Chloride	•						•						With 70 percent acid.	NFPA 1978
Wood		•											With concentrated acid.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Zinc											•		Incandescence occurs with concentrated acid and molten zinc.	NFPA 1978
Zirconium-Uranium Alloys		•											Mild explosion on contact.	NFPA 1978
CHEMICAL GROUPS														
Alcohols		•								•			Mixtures are unstable, possibly explosive and readily detonated.	Bretherick 1979
Aldehydes	•												Oxidation and gas formation occurs.	EPA 600/2-80-076
Aliphatic Amines		•											Ignition varies from immediate to several minutes.	Bretherick 1979
Alkali & Alkaline Earth Metals		•	•	•						•			Flammable hydrogen gas may be generated, reaction could be so violent as to cause fire or explosion.	EPA 600/2-80-076

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Alkanethiols	•	•											Exothermic reactions are possible.	Bretherick 1979
Amides	•					•							Oxidation and formation of toxic fumes of nitrogen oxides.	EPA 600/2-80-076
Amines	•					•							Oxidation and formation of toxic fumes of nitrogen oxides.	EPA 600/2-80-076
Anion Exchange Resins		•											Oxidative degradation of resin occurs.	Bretherick 1979
Aromatic Amines		•											Many aromatic amines ignite with red fuming nitric acid.	Bretherick 1979
Aromatic Hydrocarbon	•												Possible ignition of mixture.	EPA 600/2-80-076
Azo Compounds	•	•	•			•	•						Oxidation occurs with formation of toxic fumes of nitrogen oxides; unstable mixtures may cause explosions.	EPA 600/2-80-076

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Cation Exchange Resins	•		•						•				Oxidative degradation of resin occurs.	CE 1980c
Carbamates	•					•							Exothermic hydrolysis with possible formation of toxic fumes of nitrogen oxides.	EPA 600/2-80-076
Caustics	•									•				EPA 600/2-80-076
Combustible Materials	•	•				•	•							EPA 600/2-80-076
Cyanides			•			•							Flammable hydrogen cyanide gas may evolve.	EPA 600/2-80-076
Dithiocarbamates	•	•		•		•							Flammable carbon disulphide may evolve.	EPA 600/2-80-076
Epoxides	•	•			•								Ignition of mixtures may occur.	EPA 600/2-80-076
Esters	•					•							Possible ignition of more flammable esters.	EPA 600/2-80-076
Ethers	•	•											Exothermic acid-catalyzed cleavage may occur.	EPA 600/2-80-076

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Explosives	•		•											EPA 600/2-80-076
Fluorides	•					•							Gaseous hydrogen fluoride may evolve.	EPA 600/2-80-076
Halogenated Organics	•				•	•							Reaction may form toxic fumes of hydrogen chloride, phosgene, etc.	EPA 600/2-80-076
Hydrazines		•											Explodes or ignites most hydrazines.	Bretherick 1979
Hydrocarbons		•											Many hydrocarbons ignite on contact with concentrated acid.	Bretherick 1979
Isocyanates	•					•							Toxic nitrogen oxides may be evolved from oxidation.	EPA 600/2-80-076
Ketones	•	•											Complete decomposition will produce much heat and gas and cause fire.	EPA 600/2-80-076

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Mercaptans	•		•			•							Toxic and flammable hydrogen sulphide gas and sulphur dioxide may be formed during reaction or oxidation.	EPA 600/2-80-076
Metals (Mostly Powdered)		•	•							•			Incandescence may also occur (e.g., Mg, Ge, Ti, Zn, Mn).	Bretherick 1979
Metal Acetylides			•							•			On contact.	Bretherick 1979
Metal Powders, Vapours and Sponges	•		•	•						•			Flammable hydrogen gas can be generated.	EPA 600/2-80-076
Metal Salicylates			•										Explosion of product may occur if heavy metal ions are present.	Bretherick 1979
Metal Sheets, Rods and Drops	•	•											Flammable hydrogen gas can be formed.	EPA 600/2-80-076
Nitrides	•		•							•			Flammable ammonia gas may be generated.	EPA 600/2-80-076

8.1 **Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)**

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitriles	•		•	•			•						Formation of toxic and flammable fumes of nitrogen oxides and hydrogen cyanide gas may occur.	EPA 600/2-80-076
Nitroaromatics			•										High explosive potential for mixtures.	Bretherick 1979
Nitro Compounds	•		•			•	•			•			Toxic fumes of nitrogen oxides are produced; explosive mixtures could be detonated.	EPA 600/2-80-076
Nonmetals		•								•			Ignition occurs and possibly incandescence (e.g., B, Si).	Bretherick 1979
Nonmetal Hydrides		•	•										e.g., Ar, Ph, B, S.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Organic Acids	•												Oxidation occurs and gas formation.	EPA 600/2-80-076
Organic Materials (with fuming acids)	•	•											May cause ignition.	CPIA 1970
Organic Matter and Other Acids		•											Mixtures of the three are very explosive.	Bretherick 1979
Organic Peroxides	•		•			•							Explosive decomposition may occur during oxidation.	EPA 600/2-80-076
Organophosphates	•					•	•						Formation of toxic fumes of nitrogen oxides, sulphur oxides and phosphorus oxides may occur.	EPA 600/2-80-076
Phenols & Cresols	•												Easily oxidized.	EPA 600/2-80-076
Phosphorus Compounds		•	•										e.g., Ni or Se.	Bretherick 1979
Phosphorus Halides		•	•										e.g., Cl, Br.	Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Polyalkenes									•					Bretherick 1979
Polymerizable Compounds	•									•			Toxic fumes may result.	EPA 600/2-80-076
Reducing Agents		•	•											Bretherick 1979
Saturated Aliphatic Hydrocarbons	•												Oxidation occurs yielding heat and carbon dioxide.	EPA 600/2-80-076
Strong Reducing Agents	•	•	•							•				EPA 600/2-80-076
Sulphides										•			Toxic and flammable hydrogen sulphide gas and toxic sulphur dioxide gas can be generated.	EPA 600/2-80-076
Sulphur Halides										•			Hydrogen halide being liberated.	Bretherick 1979
Terpenes		•												NFPA 1978
Thiocyanates		•												Bretherick 1979

8.1 Compatibility of Nitric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Thioaldehydes or Thioketones										•				Bretherick 1979
Toxic Metals									•					EPA 600/2-80-076
Unsaturated Aliphatic Hydro carbons	•	•											Oxidation occurs.	EPA 600/2-80-076
Water and Water Mixtures	•													EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Nitric acid is a noncombustible material (NFPA 1978). It is a strong oxidizing agent and can react with combustible materials to cause fires. It can also react with most metals to liberate flammable hydrogen gas. Fuming acids are not combustible but the fumes liberated support combustion. Nitric acid and the fuming acids are very reactive (CPIA 1970; Merck 1983).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture and to absorb liberated oxides of nitrogen (GE 1980; ERG 1980).

Small fires:	Water, dry chemical, carbon dioxide or soda ash.
Large fires:	Flood with water.

Move containers from fire area if this can be done without risk. For massive fires, use unmanned hose holder or monitor nozzles (ERG 1980).

9.1.3 Evacuation. The following information consists of evacuation distances which appear in the literature. Important parameters suchs as spill quantity, concentration level to which evacuation level is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived to calculate hazard zones in Section 5.3 of this manual, which uses the above data. The data appearing below are derived from literature and are based on prevailing winds of 10 to 19 km/h (EAG 1978).

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

Approximate Size of Spill	Distance to Evacuate From Immediate Danger Area	Downwind Evacuation Should Be
20 m^2	60 m (78 paces)	465 m long, 320 m wide
35 m^2	90 m (120 paces)	965 m long, 465 m wide
55 m^2	110 m (144 paces)	1125 m long, 645 m wide
75 m^2	130 m (168 paces)	1290 m long, 645 m wide

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (GE 1980). Cellosize, an absorbent material, has shown possible applicability for vapour suppression and/or containment of nitric acid in spill situations (ICI 1982).

9.1.4.2 Spills on land. For small spills, cover contaminated area with sodium bicarbonate or with a mixture of soda ash/slaked lime. Mix and add water if necessary to form a slurry. Scoop up slurry for disposal and wash site with soda ash (Na_2CO_3) solution (Ashland MSDS 1977). If neutralization is not possible, soak up with sand or vermiculite and shovel into steel containers for later treatment and disposal (GE 1980).

For large spills of nitric acid, contain if possible by forming mechanical barriers to prevent spreading. Neutralize spill area with lime (CaO or CaOH) or sodium bicarbonate ($NaHCO_3$) (EPA 670/2-75-042). Calcium carbonate ($CaCO_3$) can also be used as a neutralizing agent (CG-D-38-76). Application of fly ash or cement powder to absorb the liquid bulk is also recommended (EPA 670/2-75-042). Other sorbent materials (sand, clay, earth, etc.) can also be used to absorb the spilled material (Temple 1978; Ashland MSDS 1977).

In general, it is recommended to neutralize a nitric acid spill; sodium bicarbonate ($NaHCO_3$) is suggested as giving the most efficient and fastest results. It is classed as a buffering material; the chances of increasing the pH too much as a result of an overdose is reduced. The estimated amount of sodium bicarbonate required to neutralize (reach pH of 6 and about 20 percent) a spill of nitric acid is 1.71 mole of bicarbonate for every 1 mole of HNO_3 (USDOT 1976).

It is not advisable to neutralize spills of fuming nitric acids with alkaline materials because tests indicated about 50 percent more nitrogen dioxide was evolved than with simple dilution with water. The alkaline aqueous solution used in the

experiment was composed of 5 percent sodium hydroxide (NaOH), 5 percent sodium bicarbonate ($NaHCO_3$), 5 percent sodium carbonate (Na_2CO_3) and limestone ($CaCO_3$). Water is the most effective decontaminating agent. Since concrete and asphalt contaminated with fuming nitric acids retain small amounts of acid in surface pores even after a through flushing with water, these surfaces must be further decontaminated (CPIA 1970).

When an adequate water supply is not available and where drainage is impossible, it is recommended that after removal of the bulk fuming acid the surface be sprayed with a 5 percent solution of sodium bicarbonate ($NaHCO_3$) or sodium carbonate (Na_2CO_3) until bubbling ceases. When a proper drainage system and neutralizing pit and an adequate water supply are available, complete washing down with water is sufficient. In an enclosed area, flush with large quantities of water, then spray entire surface with a 5 percent solution of sodium carbonate (Na_2CO_3) (CPIA 1970).

9.1.4.3 Spills in water. Contain if possible by forming mechanical barriers to trap the contaminated water. Neutralize with lime or sodium bicarbonate (EPA 670/2-75-042). Calcium carbonate and soda ash should also be considered as neutralizing agents (CG-D-38-76).

9.1.5 Cleanup and Treatment.

9.1.5.1 General. For treatment of contaminated water, neutralization (to pH 7.0) with a mixture of (50/50) soda ash/slaked lime followed by gravity separation of solids is recommended. Water may be added to the effluent to reduce the nitrate concentration (EPA 600/2-77-227).

9.1.6 Disposal. Waste nitric acid must never be discharged directly into sewers or surface waters. Following neutralization, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill. Various neutralization procedures are mentioned above.

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be nitric acid or a fuming nitric acid:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing

necessary to prevent any possibility of repeated or prolonged skin contact with liquid nitric acid or liquids containing nitric acids (NIOSH/OSHA 1981).

- Splash-proof safety goggles are also recommended where there is any possibility of liquid nitric acid or solutions containing nitric acid contacting the eyes (NIOSH/OSHA 1981).
- The following are permeation test results of clothing materials (Little 1983):

Material showing breakthrough at times of	Nitric Acid Concentration		
	< 30 Percent	30-70 Percent	> 70 Percent
	Natural rubber		
>1 h	Neoprene, Nitrile, Polyvinyl chloride	Neoprene, Polyvinyl chloride	-
≈1 h	Butyl rubber, Polyethylene, Chlorinated polyethylene, Styrene-butadiene rubber, Viton, Nitrile-butadiene rubber	Natural rubber, Nitrile, Nitrile with PVC, Polyethylene, Polyurethane, Viton	Natural rubber, Neoprene, Nitrile, Polyethylene, Chlorinated polyethylene, Polyvinyl chloride, Viton
<1 h		Polyvinyl alcohol	Butyl rubber, Nitrile with PVC, Polyurethane, Polyvinyl alcohol

- Neoprene and PVC are recommended for gloves (Ashland MSDS 1977). Vinyl-coated gloves are recommended for the fuming acids (CPIA 1970).
- Rubber boots are recommended to be used when handling nitric acid (MCA 1961). Rubber boots may be used with the fuming acids; however, these must be washed quickly after contact to avoid reaction, penetration, or even burning (CPIA 1970).
- PVC is recommended as a chemical suit material for protection (excellent resistance) against nitric acid (EE-20).
- Nonimpervious clothing which becomes contaminated with nitric acid should be removed immediately and not reworn until the nitric acid is removed from the clothing (NIOSH/OSHA 1981).

- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1980).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where nitric acid is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 5 mg/m^3
Particulate or Vapour Concentration	
250 mg/m^3 or less	A chemical cartridge respirator with full facepiece providing protection against nitric acid.**
	A gas mask with a chin-style or a front- or back-mounted organic vapour canister providing protection against nitric acid.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 250 mg/m^3*** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied air-respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask containing nonoxidizable sorbents and providing protection against nitric acid.
	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** Nitric acid is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials such as activated charcoal and therefore should not be used to provide protection against nitric acid. Only nonoxidizable sorbents are allowed.

*** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric acid; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 250 mg/m^3, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 Storage Precautions. Store in a clean, cool, well-ventilated area, away from organic chemicals, strong bases, metal powders, carbides, sulphides, and any readily oxidizable material. Protect from direct sunlight. Protect against physical damage.

Nitric acid (also the fuming acids) is a corrosive material and will attack skin, metals and many organic substances. The nitrogen oxides produced from the acid are all toxic, and proper ventilation should always be used. Neutralizing and absorbing materials such as soda ash and sand should be readily available to areas of use and storage of nitric acid. Electrical fixtures should be vapour-proof (GE 1980).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Leak Plugging	Plug N' Dike*
Leak Plugging	NRC Tantalum Patch Kits
Temporary Storage	Portable Collection Bag System
Treating Agents	Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information. No spill experiences are included for nitric acid as no documentation could be found.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

The presence of acid in a given sample can be determined, quantitatively or qualitatively, by conventional titration using phenolphthalein as the indicator for the former and pH or litmus paper for the latter. This, of course, is not specific for nitric acid; if other acids are known to be or suspected of being present, the procedure must be supplemented by the test specific for nitrate ion. Qualitatively, the nitrate ion in water (or soil after extraction) can be detected by the classical brown-ring test, the copper-turnings test, the reduction of nitrate to ammonia by active metal or alloy, or the nitrogen precipitation test. Air samples can be easily tested with a Drager tube. With respect to quantitative procedures, many methods are available.

11.1 Quantitative Method for the Detection of Nitric Acid in Air

11.1.1 Specific Ion Electrode (NIOSH 1978). A range of 2.60 to 10.8 mg/m^3 (1.01 to 4.19 ppm) of nitric acid as nitrate ion may be determined using an ion specific electrode. A known volume of air is drawn through a midget impinger containing 20 mL of distilled water. A sample size of 180 L at a flow rate of 1.0 L/min is recommended.

The sample is transferred to a 25 mL volumetric flask and a 5 mL aliquot of buffer solution is added. The buffer is prepared by dissolving 4.3 g of aluminum sulphate, 1.6 g of boric acid, 3.9 g of silver sulphate, and 2.4 g of sulphamic acid in distilled water

and diluting to 500 mL. The sample is diluted to a volume of 25 mL with distilled water and transferred to a 50 mL beaker containing a magnetic stirring bar. A suitable nitrate ion specific electrode and reference electrode are immersed in the sample solution and the millivolt reading recorded. The nitric acid is determined using a calibration curve plotted on semilogarithmic paper.

11.2 Qualitative Method for the Detection of Nitric Acid in Air

A range of 1 to 50 ppm nitric acid in air may be determined using a Drager detector tube for nitric acid.

A known volume of air is drawn through a Drager detector tube for nitric acid using a Drager multi-gas detector pump. A colour change of the blue indicating layer to yellow indicates nitric acid. The colour change is based on the reaction between nitric acid and bromophenol blue (Drager 1979).

11.3 Quantitative Method for the Detection of Nitric Acid in Water

11.3.1 Colourimetric (ASTM 1979). A range of 1 to 50 mg/L (ppm) of nitric acid as nitrate ion may be determined colourimetrically. Nitrate ion reacts with brucine in strong sulphuric acid solution to develop a yellow colour. Even though the colour does not follow the Beer-Lambert relationship, a plot of absorbance versus concentration produces a smooth curve. It is necessary, however, to develop a series of standards simultaneously with the samples.

A minimum volume of 2 L of representative sample is collected in an appropriate container. The determination may be interfered with by the presence of strong oxidizing or reducing agents. The presence of the former may be determined with orthotolidine $(C_6H_3(CH_3)NH_2)_2$ (an example is chlorine). Other interferences include organic matter in high concentration and nitrite ion. The presence of chlorine will produce a yellow colour, as will other oxidizing agents. The orthotolidine reagent is prepared by dissolving 1.35 g of orthotolidine dihydrochloride in 500 mL of distilled water. Add this solution, with constant stirring, to a mixture of 350 mL of distilled water and 150 mL of concentrated hydrochloric acid. The solution should be stored in brown bottles and protected from direct sunlight. The solution is good for 6 months. It must be stored at room temperature and never allowed to fall below 0°C. It must not come in contact with rubber. The material is toxic; do not ingest or breath vapours. The test can be made using spot plates. After a 1 mL sample is added to about 3 drops of orthotolidine solution,

the colour will develop within 1 min and fade thereafter. The minimum readable colour is produced by a chlorine concentration between 0.05 and 0.1 mg/L (Taras 1971).

If residual chlorine is determined to be present, add, with mixing, 0.1 mL of arsenite solution to a 50 mL portion of sample for each 0.05 mg/L of chlorine. Add one drop in excess. If the water is turbid or has a high organic matter (colour), remove by adding 0.5 g of specially treated activated carbon and 3 mL of aluminum hydroxide cream to 150 mL of sample. Mix well, allow to stand for a few minutes, and filter, discarding the first portion of the filtrate (I).

The arsenite solution is prepared by dissolving 1.83 g of sodium arsenite ($NaAsO_2$) in 1 L of water. This material is toxic and ingestion must be avoided. The activated carbon is specially prepared by heating fine grain (0.2 to 0.5 mm diameter) activated carbon to red heat in a carbon dioxide atmosphere. The material is then cooled, extracted with n-hexane and washed with water at 80°C. Finally, the aluminum hydroxide cream is prepared by dissolving 124 g of potassium or aluminum alum ($Al_2(SO_4)_3 \cdot K_2SO_4$ or $Al_2(SO_4)_3$) in 1 L of water. Heat to 50°C and slowly add 55 mL of aqueous ammonia (NH_4OH, sp. gr. 0.90) with stirring. Let stand 1 hour, and then wash the precipitate with water by mixing and decanting until free of ammonia, chloride, nitrate and nitrite ions. Simple qualitative tests will determine the latter.

A 5.0 mL sample of the filtrate (I) or of the clear, colourless water (no turbidity or organic matter) containing not more than 50 mg/L of nitrate ion is transferred into a clean, dry 50 mL beaker. A 1.0 mL sample of brucine-sulphanilic acid reagent is added. The latter is prepared by dissolving 1 g of brucine sulphate ($(C_{23}H_{26}N_2O_4)_2H_2SO_4$) and 0.1 g of sulphanilic acid ($C_6H_7NO_3S$) in about 70 mL of hot water. A 3 mL volume of hydrochloric acid (sp. gr. 1.19) is added, and the solution cooled and diluted to 100 mL with water. This reagent (brucine sulphate) is toxic and ingestion must be avoided.

To a second 50 mL beaker are added 10 mL of sulphuric acid solution which was prepared by carefully adding 500 mL of sulphuric acid (sp. gr. 1.84) to 75 mL of water. It is important to keep the sulphuric acid reagent tightly stoppered to prevent absorption of moisture. The contents of the beaker containing the brucine-sulphanilic acid reagent is carefully added to the beaker containing the sulphuric acid. The contents must be thoroughly mixed. The colour is allowed to develop in a dark location for 10 minutes, after which 10 mL of water are added to the sample, mixed, and allowed to cool for 20 to 30 minutes in a dark location.

The absorbance of the sample is measured at 410 nm against a blank reagent using a suitable spectrophotometer and 1 cm matched cells. The blank is treated similarly to the sample, but the brucine-sulphanilic acid reagent is omitted. The nitric acid is determined using a freshly prepared calibration curve developed from a series of standard solutions. The standard solution is prepared by dissolving 1.631 g of dried potassium nitrate (KNO_3) in 20 mL of water and diluting to 1 L. The solid is dried at 105°C for 24 h. One millilitre of standard is equal to 1 mg NO_3^-. The nitrate ion concentration is read directly from the calibration curve, in mg/L.

11.4 Qualitative Method for the Detection of Nitric Acid in Water

The sample is collected as in Section 11.3.1. A 1 mL volume of sample is placed in a test tube and 3 M sulphuric acid is added, dropwise, until the sample is acid. Dropwise addition of 0.5 M silver perchlorate ($AgClO_4$) is continued with stirring until precipitation is complete. A 3 mL volume of 1 M ferrous sulphate ($FeSO_4$) solution is added and the solution centrifuged if any precipitate forms. The supernatant is decanted into a test tube and cooled under water. The test tube is held at an angle and concentrated sulphuric acid is slowly poured down the sides of the test tube. A 1 in. layer of acid at the bottom of the test tube is sufficient. A thin brown ring at the junction of the two liquids indicates the presence of nitrate (Welcher 1955). The brown colour is a result of the formation of the ferrous nitroso ion ($FeNO^{++}$). Nitric oxide (NO) is formed by reduction of nitrate ion by ferrous ion (Sienko 1961).

11.5 Quantitative Method for the Detection of Nitric Acid in Soil

11.5.1 Titrimetric (Hesse 1972). A variable range of nitric acid as nitrate ion, depending on the aliquot of extract used, may be determined by steam distillation followed by titration.

A 5 g sample of 2 mm soil (sieved through a 10-mesh screen) is shaken for 60 min with 50 mL of 2 M potassium chloride solution and allowed to settle. The potassium chloride solution, upon preparation, should be boiled for 15 min with solid magnesium oxide to remove any ammonia, cooled, filtered, and then diluted to 50 mL. A suitable aliquot of potassium chloride extract is transferred to a distillation flask. A boric acid solution is prepared by dissolving 20 g boric acid in 900 mL of hot water and adding 20 mL of mixed indicator.

The indicator is prepared by dissolving 0.1 g of bromocresol green and 0.07 g of methyl red in 100 mL of ethanol. Sodium hydroxide (0.1 M) is added dropwise until a

reddish purple colour is obtained. The volume is taken to 1 L. A 5 mL aliquot of the boric acid solution is transferred to a suitable conical flask beneath the condenser which is attached to the distillation flask.

A 0.5 g mass of magnesium oxide and 0.2 g mass of Devardas' alloy are added to the distillation flask and the flask rapidly stoppered. Devardas' alloy is prepared by combining copper, aluminum, and zinc in the weight ratio of 50/45/5. The alloy should be finely ground to pass a 0.15 mm sieve. The contents are steam distilled into the boric acid solution. A 30 mL volume of distillate is collected and titrated with standardized hydrochloric acid.

11.6 Qualitative Method for the Detection of Nitric Acid in Soil

The sample is collected and extracted as in Section 11.5.1 and the test as outlined in Section 11.4 is carried out. The formation of a brown ring indicates the presence of nitrate ion.

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight